



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
-----------------	-------------	----------------------	---------------------	------------------

09/832,141

04/09/2001

John W. Chrisman III

4826US

8520

7590 09/12/2007
BRICK G. POWER
TRASK, BRITT & ROSSA LAW OFFICES
P.O. BOX 2550
SALT LAKE CITY, UT 84110

EXAMINER

PIERCE, WILLIAM M

ART UNIT

PAPER NUMBER

3711

MAIL DATE

DELIVERY MODE

09/12/2007

PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.



UNITED STATES PATENT AND TRADEMARK OFFICE

Commissioner for Patents
United States Patent and Trademark Office
P.O. Box 1450
Alexandria, VA 22313-1450
www.uspto.gov

**BEFORE THE BOARD OF PATENT APPEALS
AND INTERFERENCES**

Application Number: 09/832,141
Filing Date: April 09, 2001
Appellant(s): CHRISMAN, JOHN W.

**MAILED
SEP 12 2007
GROUP 3700**

Brick Power
For Appellant

EXAMINER'S ANSWER

This is in response to the appeal brief filed 5/15/07 appealing from the Office action mailed 6/30/06.

(1) Real Party in Interest

A statement identifying by name the real party in interest is contained in the brief.

(2) Related Appeals and Interferences

The case as been previously appealed on 4/17/03 with a subsequent Examiner's Answer. Appellant filed on RCE 6/28/05 prior to any Decision by the Board. The examiner is not aware of any other related appeals, interferences, or judicial proceedings which will directly affect or be directly affected by or have a bearing on the Board's decision in the pending appeal.

(3) Status of Claims

The statement of the status of claims contained in the brief is correct.

(4) Status of Amendments After Final

The appellant's statement of the status of amendments after final rejection contained in the brief is correct.

(5) Summary of Claimed Subject Matter

The summary of claimed subject matter contained in the brief is correct.

(6) Grounds of Rejection to be Reviewed on Appeal

The appellant's statement of the grounds of rejection to be reviewed on appeal is correct.

(7) Claims Appendix

The copy of the appealed claims contained in the Appendix to the brief is correct.

(8) Evidence Relied Upon

4,722,815	Shibanai	2-1988
4,762,493	Anderson	8-1998

4,293,602

Coffey et al.

10-1961

(9) Grounds of Rejection

The following ground(s) of rejection are applicable to the appealed claims:

Claims 1-3, 5, 7, 8, 10-27, 29 and 31 are rejected under 35 U.S.C. 103(a) as being unpatentable over what is old and well known in bowling balls in view of Shibantai and Coffey.

As to claims 1-3, 5, 7, 10-19, 20-27, 29 and 31, bowling balls of nonporous polymeric two-part thermosetting resin is old and well known. This is admitted old at the bottom of pg. 2 of Appellant's specification. Lacking in bowling balls is the use of a fragrance. However, perfumed additives and perfumed polymers intended for the purpose of making plastic articles with a fragrance are also well known. Shibantai teaches compounds to be included in synthetic resin products in order to enhance their smell. He clearly teaches the use of epoxy (col. 7, ln. 56) which is known in the art to be available as a one-part or two-part resin. While there is no direct teaching of using his compound in a bowling ball, it has been held that, in evaluating a reference, it is proper to take into account not only the specific teaching of the reference(s) but also the inferences which one skilled in the art would reasonably be expected to draw therefrom. In re Preda, 401 F.2d 825, 826, 159 USPQ 342,344 (CCPA 1968). Additionally, one must observe that an artisan must be presumed to know something about the art apart from what the references disclose (see In re Jacoby, 309 F.2d, 513,516, 135 USPQ 317, 319 (CCPA 1962). In line with this, one skilled in the art would clearly have found it obvious to have applied perfumed compounds, such as Shibantai's in order to make a bowling ball smell better. Where the claims call for a two-part resin and the fragrance being dissolved therein, Shibantai directly teaches (col. 7, ln. 56) that smell can be added to "epoxy resin coatings". Epoxy resin is a known "two part" resin. See evidence in the copy of Handbook of Reinforced Plastics, "Epoxy Resins", pg. 71, col. 1, ln. 20, appended to this Answer, where it shows that "cure may be established using materials classed as hardeners or curing agents". Shibantai also teaches that "it is also possible to mix perfume...with a synthetic resin compound followed by molding" (col. 1, ln. 26) but that this "direct addition of perfume...to synthetic resin compound

is not as effective as it seems" (col. 1, 35). Hence Shibantai goes on to teach an improved more effective method of adding fragrance to a product that includes forming an inclusion compound consisting of perfume included in cyclodextrin. While Shibantai does not detail the old and known methods of "mixing perfume" and "direct addition of perfume" that is at least partially dissolved within the resin, such are considered old when one further considers Coffey et al. as an example. Coffey teaches that it is an old expedient and would have been obvious to mix fragrances to two part resins in the forming of a fragrances polymer product. Edwards and Wilbert, are further examples of direct mixing of fragrances with a polyurethane prior to molding. The art is replete with the successful addition of fragrance to two part polymer products. The motivation is simply to "impart to other polymeric products pleasant odors" (Wilbert, col. 1, ln. 57). The amount of fragrance as called for in claim 8 is considered an obvious matter of choice depending upon how strong of a smell is desired. The examiner's position is in line and fully supported by the findings of the Courts in the recent decision to *KSR Int'l Co. v. Teleflex, Inc.*, No 04-1350 (U.S. APR. 30, 2007).

Claims 9, 32 and 33 are rejected under 35 U.S.C. 103(a) as being unpatentable over bowling balls in view of Shibantai and further in view of Anderson.

Applying a pigment to polymer resin products to give them color is old and well known. Anderson teaches that it is old to apply a color that correlates to a fragrance in a product. To have done so with a bowling ball would have been obvious to one skilled in the art for the novelty.

(10) Response to Argument

(B) Rejection under 103

(1) and (2)

Appellant remarks pertaining to the "applicable law" and his interpretation of the references on pgs. 6-8 with no further response deemed necessary.

(3)

Appellant's assessment of a "two-part resin" is not complete and in line with what is disclosed in his specification. Appellant is not entitled at this point to change the meaning by stating that two-part is intended to mean what is known in the polymer art in attempts to evade the applied art. *ACTV, Inc. v. The Walt Disney Company*, 346 F.3d 1082, 1092, 68 USPQ2d 1516, 1524 (Fed. Cir. 2003) sets forth that where there was no expressed definition given for the term in the specification, the term should be given its broadest reasonable interpretation consistent with the intrinsic record and take on the ordinary and customary meaning attributed to it by those of ordinary skill in the art. The question here is are those of ordinary skill in the art bowlers or polymer scientists? Here the broadest reasonable interpretation of "two-part" is considered customary to one skilled in the art of bowling. Most broadly "two-part" would be given its ordinary meaning of a resin having two parts, a first part and a second part. This interpretation is commensurate with what appellant meant by two-part in his discussing of his invention in his specification where it conveys most broadly that any plastic made up of two components can be considered a "two-part resin". Specifically, the specification notes that "conventionally, bowling balls have been formed from machineable, thermosetting plastic materials." (pg. 2, [0002]) and at paragraph [0004] of pg. 2 discusses reactive polymers that require the presence of a catalyst for polymerization requiring only an A-side and a B-side (i.e. two parts). Nowhere in the specification does appellant consider or define polymers requiring a catalyst (such as the ones discussed in paragraph [0004]) to be defined as "two-part resins" that require "mixing" as alluded to in his Brief. From appellant's specification, he has defined a two-part resin to be broader than what is commonly referred to in the industry. From his specification, a "two-part resin is most broadly one having an "two parts", an A-side and a B-side. His definition of a "two-part resin" used for his invention fits what is commonly referred to in the plastics industry as a "one-part resin" because these resins are known to require a second part or curing agent in addition to their base component. (See pg. 2, col. 1, ln. 8, of Three Bond Technical News, One-Part Epoxy Resin at <http://www.threebond.co.jp/en/technical/technicalnews/pdf/tech19.pdf> appended to this Answer). Since appellant's specification never compares and contrasts the differences between one and two part resin or specifically discloses that his invention is only drawn to a two-part resin that is conventionally used, his

Art Unit: 3726

later use of the term-two-part resin is any resin most broadly having two parts and A-side and a B-side, which encompasses both "one-part" and "two-part" resins known in the plastics art since they are known to use the same epoxy resins and a curing agent. Both require mixing and blending of the two components. The difference is that one-part resin can be considered to be a "premixed" compound and two-part resin must be mixed just before manufacture. (See <http://www.adhesivestoolkit.com/Data/AdhesiveTypesOverview.xtp> that states;

"Two-part epoxy adhesives start to react under ambient conditions once the two components have been mixed together and are often termed room-temperature (RT) curing adhesives because of this. The reaction mechanism is still affected by temperature and as a rule of thumb the reaction rate approximately doubles for every 10°C rise in temperature i.e. an epoxy which takes 1 hour to cure at 20°C, will cure in 15 minutes at 40°C. Conversely the cure time will double as the temperature drops by 10°C. Complete cure times at ambient temperatures for two-part systems range from ~10mins to several days.

Single-part epoxy adhesives are available in liquid, paste or film form. These adhesives require heat to cure. The resin and catalytic hardener are pre-mixed but curing does not occur because the catalyst is in an inactive form at room temperature. It only becomes reactive as the temperature is raised, usually in excess of 100°C. The higher the temperature, the faster the reaction becomes and hence shorter curing times of less than ten minutes can be obtained. Cure of the two-part adhesives can also be accelerated by heat."

Appellant in response to the first office action and the applied art added the term "two-part" to his claims and attempts to use the "ordinary meaning" in the plastics art to distinguish from the teaching references. Here he is attempting to persuade the Board that the scope of his claims is to a "two-part resin" defined by its conventional meaning used in industry and not the "two-part" resin as he disclosed throughout his specification. As set forth above, appellant has defined in his specification that to be a "two part resin" it only need to have and A-side and a B-side which includes both "one-part" and "two-part" resins commonly known in the art. One skilled in that art here is an ordinary bowler. Clearly, he would not be versed in plastics and the science surrounding polymers. Reading appellants specification, he would not conclude that his invention was drawn to a "two-part resin" as is conventionally used in the art of polymers. Instead, conveyed to him from appellant's specification would be that any plastic having an two parts, an A-side and B-side is required. Hence, for the purposes of this rejection, the broadest interpretation is, that the prior art regardless of whether it teaches a one-part or two-part resin as

commonly referred to in the polymer art, it meets the limitation of the claims where the resin used is comprise of more than one component.

Regardless of the interpretation of the scope afforded to the term two-part used in the instant claims, Shibantai is considered to most broadly disclose a "two-part" resin even in line with what one skilled in the art of polymers considers such to be. He discloses a "synthetic resin compound and glycidol(s)" (col. 17, ln. 51). Appellant's conclusion on pg. 9, ln. 12 of the Brief that "Shinbantai do not require mixing" is in error. At col. 3, ln. 66, Sinbantai explicitly teaches "mixing with various synthetic resin materials...". Where he states that Shibantai is "limited to one-part thermoplastic resins..." he is misleading the Board. More aptly, he directly teaches (col. 7, ln. 56) that smell can be added to "epoxy resin coatings". Epoxy resin is a known "two part" resin. See evidence in the copy of Handbook of Reinforced Plastics, "Epoxy Resins", pg. 71, col. 1, ln. 20 where is shows that "cure may be established using materials classed as hardeners or curing agents". Appellant submitted NPL on 6/17/2003 to "Two-Part Sculpting Epoxies" further shows that epoxies are known to be two part polymers as called for by the claims.

With respect to Coffey, he suggests fragrances most broadly to "synthetic resins" (col. 1, ln. 11). He goes on to describe a preferred embodiment with "fluorocarbon resin" (col. 2, ln. 60). From U.S. Patent 4,314,004 to Stoneberg we see that fluorocarbon resins are formed by a reaction with a second part (col. 2, lns. 54-68) making them what can be considered a two-part resin. As such both Shinbantai and Coffey are not limited to only one part resins. Their disclosure is much broader and clearly suggest a two-part resin as called for by the claims.

Lastly, using a one-part or two-part resin have known properties with known advantages and disadvantage to one skilled in the art of polymers and resins can be formulated to be either one-part or two- part depending upon the requirements of the products to be made. For example, polyurethane can be either a one-part or a two-part polymer. See appellants NPL to "One and Two-Part Resin Systems" of 6/17/2003 for example. One skilled in the art would clearly expect a fragrance inclusion additive to work in both a one-part and a two-part resin, as understood in the polymer art, equally the same. This selection of a known material to take advantage of its known properties has been held obvious.

Obviousness of Claimed Invention Fairly taught.

First, a bowling ball that comprises a mass with a "two-part" resin as well as a polyol is old as admitted by appellant respectively on the bottom of pg. 2 of his specification and pg. 10, ln. 6 of his Brief. The base reference is applicant's own specification and what is admitted as old. The grounds for rejection recognizes that Shinbanai and Coffey do not teach the specific details of making a bowling ball. These teaching references are relied on for what they disclose about adding fragrance to products like a bowling ball made of two-part resins to make them smell better. The only thing missing from the prior art of bowling balls is the addition of fragrance to the resins used to make them. Both Shinbanai and Coffey fairly suggest adding fragrance to resins to impart smell to the product. Clearly one faced with the problem of wanting a bowling ball to smell more appealing would consider the teachings of these references.

As to claim 20, skill has to be presumed on the part of a person practicing the invention of Shinbanai. Known is that once the catalyst is added to polyol, there a "working time" for the resin is set when working with a two-part resin known in the polymer art. Mixing the fragrance into the polyol, the main fundamental ingredient thereof, prior to the catalyst does nothing more than what would be obvious to the skilled artisan. *KSR Int'l Co. v. Teleflex, Inc., No 04-1350 (U.S. APR. 30, 2007)*. Further, it is clear that the fragrance could be added to the polyol after the addition of the catalyst. However, it would need to be done such that it could be uniformly mixed and molded before polymerization were to begin. Clearly appellant is claiming nothing more than the use of known techniques that are inherent in the prior art.

As to claims 20 and 21-26, the removal of gas "trapped" in a polymer mixture is old and inherent in the art of plastics. Failure to do so results in an inferior final product made by the visibility of "bubbles" that art trapped after the product has fully cured. Surely applicant is not the inventor of removing trapped air or gas known throughout the plastics industry. See U.S. 6,525,125, col. 10, ln. 55 which discloses a resin for production of bowling balls and removing of gas bubbles under a vacuum at col. 11, ln 63. On pg. 8, [0032] of his specification, appellant admits to the use of a vacuum, as well as "any known techniques".

With respect to claim 21, Shinbanai discloses mixing fragrance inclusion compounds (col. 2, ln. 45) "with a synthetic resin coating" (col. 3, ln. 57) for "direct addition of perfume(s)... to a synthetic resin compound" (col 1, ln. 35). He discloses "epoxy resin" (col. 7, ln. 56) which is a broad category of known polyols. Polyol in the method of manufacturing of a bowling ball is old. This is admitted by appellant on his specification, paragraph [0004]. To further assist the Board in making its determination and to appropriately determine what is known in the art, the examiner has appended two websites that discuss the uses of polyol with respect to polyurethanes. Note <http://www.kosa.com/poly/specprod.htm> and <http://polyol.synair.com/AbOut%20Polyols.htm>, copies of which are appended to this examiners answer. As to claim 21, Webster's New World Dictionary defines "dissolve" as "to merge with a liquid". Shinbanai clearly teaches a fragrance that is to be "merged" with a liquid polymer

As set forth above, a catalyst is well known as being used with polyols to cause polymerization. The use of a catalyst as called for in claim 23 is not new to the art of plastics.

The use of isocyanates as called for by claim 24 is old. The Boards attention is drawn to pg. 5 of copies the *Handbook* appended to this Answer. As mentioned previously in the Answer, they are mostly known for having a "foaming" affect on plastic compositions.

Motivation to Combine

As set forth in the final office action sufficient motivation to combine the teachings of Shinbanai and Coffey with bowling balls two-part polyurethane bowling balls, admittedly old and well known, in order to give them a better smell. Where both polyurethane bowling balls are known in the art and "fragrance inclusion compounds" for products made of a resin such as polyurethane, it is clear that appellant did not "invent" adding a fragrance to a bowling ball. Instead he took know materials such as a fragrance inclusion compound and applied it for its intended purpose of imparting smell to a final product.

The controlling principles of the Law of Obviousness here resides in *KSR Int'l Co. v. Teleflex, Inc.*, No 04-1350 (U.S. APR. 30, 2007) and not in whether there is an explicit teaching suggestion or motivation as implied by appellant. Here, in line with *KSR*, we have a clear cut situation before the Board where appellant's improvement is nothing "more than the predictable use of prior art elements according

to their established functions" and merely combined prior art elements according to known methods to yield predictable results. Clearly, fragrance inclusion products and methods that have been applied in the art to be known to work on other polymer resin products would be expected to work on a bowling ball made of similar polymers. The level of ordinary skill necessary to recognize the results is low. Here one can see of record no new or different function of the bowling ball of the instant invention and the results of adding fragrance to a polymer in a bowling ball give the predictable results of having the bowling ball smell according to the fragrance added.

KSR further supports the examiner's position where appellant has merely used known techniques of adding fragrance to polymers used in articles made of plastic to improve to improve similar articles made of plastic, such as a bowling ball. The addition a fragrance inclusion, such as that taught by Shinbanai and Coffey, into a plastic product would have clearly been well within the skill of one of ordinary skill in the art of plastics. The results of making any plastic product that such a fragrance is applied to smell better is considered expected and predictable. Here we have the situation where appellant has done nothing more than applied known techniques of including a fragrance into a plastic resin product to yield a predictable outcome with only common tools of the trade.

Here the rejection does not suggest to "modify the teachings of Shinbanai and Coffey" (Brief, pg. 12, ln. 3). The rejection suggests modifying known two-part polyurethane bowling balls, admitted old by appellant at the bottom of pg. 2 of his specification, using the products and techniques known in the art as suggested by Shinbanai and Coffey. One would clearly recognize that known techniques for imparting a fragrance in plastic products would yield the same results in other products made of similar polymer materials.

In order to make a rejection tenable, there is no requirement that one skilled in the art would need to be aware of "any demand for scented bowling balls" (Brief, pg. 12, ln. 15). Here the scenting of the bowling ball is nothing more than a novelty as is recognized in the art of adding a scent to other products. One wishing to add the same novelty of smell to a product such as a bowling ball would surely consider how this novelty was practiced in other articles made of similar polymers.

In the middle of pg. 13, appellant asserts that the fragrance added to the bowling ball yields unpredictable results by increasing friction and the "hooking ability" of the ball. First, the hooking potential of a ball is controlled by the design features of the ball such as the shape, weight design and placement of core material and the type of coverstock used on the ball. There is no evidence that it is merely the addition of fragrance that would give the ball any better performance and that the performance may not be attributed to another feature of the ball. In the article of record provided with the affidavit of 6/28/05, *Fragrances Add Some Zest to Bowling Balls*, appellant appears to point to a quote by "Steve Kloempken, the company's technical director, says computer tests indicate that the aromatic chemicals give Storms balls a bit of extra hook". However, this statement is not substantiated by any evidence of record such as the computer test to which he refers. Here appellant has not shown where identical balls, with the exception of one without fragrance and another with, will perform any different. Lastly, upon review, nowhere in the specification does it mention an increased hooking potential.

Secondary Considerations

Appellant argues that "the commercial success of Storm's scented bowling balls may be attributed to the incorporation of the fragrance therein" (bottom pg. 14). The fact that the commercial success MAY only be attributed to the added fragrance is the reason that the secondary considerations have been unpersuasive. The declarations provided only contained conclusions without establishing a nexus between those conclusions with and any supporting evidence to the scope of the instant claims. In essence, they amount to an opinion that is considered of limited probative value with regard to rebutting a prima facie case. *In re Grunwell*, 609 F.2d 486, 203 USPQ 1055 (CCPA 1979); *In re Buchner*, 929 F.2d 660, 18 USPQ2d 1331 (Fed. Cir. 1991). The burden is upon appellant to show a clear nexus between the commercial success and the claimed invention which has not been done. The Federal Circuit has acknowledged that applicant bears the burden of establishing nexus, stating:

In the ex parte process of examining a patent application, however, the PTO lacks the means or resources to gather evidence which supports or refutes the applicant's assertion that the sales constitute commercial success. C.f. *Ex parte Remark*, 15USPQ2d 1498, 1503 ([BPAI] 1990) (evidentiary routine of shifting burdens in

Art Unit: 3726

civil proceedings inappropriate in ex parte prosecution proceedings because examiner has no available means for adducing evidence). Consequently, the PTO must rely upon the applicant to provide hard evidence of commercial success. In re Huang , 100 F.3d 135, 139-40, 40 USPQ2d 1685, 1689 (Fed. Cir. 1996). See also GPAC, 57 F.3d at 1580, 35 USPQ2d at 1121; In re Paulsen, 30 F.3d 1475, 1482, 31 USPQ2d 1671, 1676 (Fed. Cir. 1994)

The examiner has considered the Declaration of John Chrisman and has determined that the commercial success of the Storm bowling ball has not been shown to be linked to the claimed invention. First, the "scent" has been referred to as a "gimmick" which is in all likelihood linked to a heavy advertising and promotional budget. Nothing of record shows that the increased sales in 2001 for Storm was not linked to greater promotion or endorsements of its products or other products popular in its product line rather than to the scenting of the balls itself. Non-obviousness is not shown by a brilliant marketing strategy that includes press releases and recognition from the novelty of the ball. Second, the balls of Storm sell because they perform well. It is the overall design and performance of the ball that has resulted in its success and not the mere addition of a fragrance. Examiner is not convinced that top bowlers would buy the Storm ball merely because it smells good. It the top performance characteristics of the ball that is attributed to the success of the company and the sales of its balls. Moreover, the article in eMediaWire state that the balls of Storm were discounted with a "savings of over 30%". Clearly discounting sales can lead to the commercial success of a product. Lastly, it has further not been shown that Storm products are not being priced cheaper than the competition or with buying incentives that account for the percentages of growth in sales being claimed.

Where appellant alleges a "great deal" of commercial success even though the balls have been sold for 10% more than comparable balls, he has not qualified what is considered to be a "great deal" and a "comparable balls". Note that he did not say that the ball sold for 10% more than for "identical" unscented balls. Clearly, colors, advertising, discounts, better performance, new endorsements and the like can easily account for an 10% increase in sales price. Likewise, appellant does not qualify to what "30% share of their market segment" pertains. Is this the market segment of identical unscented balls? Do they even offer identical unscented balls? Clearly, no nexus has been established and the evidence of secondary consideration is unpersuasive.

(b) SHINBANAI, COFFEY AND ANDERSON

Appellant argues that the rejected claims are allowable base on their dependency of the claims argued above. Examiner's position is set forth above and no further comment is deemed necessary.

(11) Related Proceeding(s) Appendix

No decision rendered by a court or the Board is identified by the examiner in the Related Appeals and Interferences section of this examiner's answer.

For the above reasons, it is believed that the rejections should be sustained.

Respectfully submitted,

/William M. Pierce/ Primary Examiner 3711

Conferees:

/Marc Jimenez/ TQAS TC 3700

/Gene Kim/ Supervisory Patent Examiner 3711



HANDBOOK OF REINFORCED PLASTICS

of The Society of The Plastics Industry, Inc.

SAMUEL S. OLEESKY

*Consultant for Reinforced Plastics
Los Angeles, California*

and

J. GILBERT MOHR

*Johns-Manville Fiber Glass Division
Pittsfield, Ohio*

SCIENTIFIC LIBRARY

AUG 6 1953

U.S. PATENT OFFICE



VAN NOSTRAND REINHOLD COMPANY

NEW YORK CHICAGO TORONTO LONDON MELBOURNE

Chapter 1-1

WHAT ARE REINFORCED PLASTICS?

A complete understanding of the field of Reinforced Plastics is almost impossible without a basic knowledge of the plastics industry as a whole. Briefly speaking, plastics are materials, generally of high molecular weight and of indefinite molecular complexity, whose form and/or properties may be transformed into useful shapes or articles by the techniques of applying heat, pressure, or other manufacturing procedures. Still joining with a broad brush, we may divide plastics into two general categories, the thermoplastics and the thermosets.

Many examples have been used to illustrate the differences between these two groups, none of which hold completely. For example, thermoplastics have been compared with candles, while thermosets have been compared with eggs. That is, a candle (thermoplastic) may be shaped, melted, reshaped, and so on, until the molder has exhausted his possibilities. The egg, however, having once been cooked hard, cannot be "uncooked." This is the picture given to the layman, and it suffices as a general method of differentiating between the groups.

But for someone who wants to design or manufacture articles from these wonderful materials, so simple a division is not sufficient. Particular properties of each material must be known, so that intelligent use may be made of it and, most important to the plastics industry, minimum waste may be avoided.

Following is an alphabetical list of currently available plastic groups and a brief examination of each with respect to its properties and uses.

Acetal Resins

This resin, a thermoplastic, was introduced commercially in 1929. According to its producers, it is said, among the good design properties, is excellent and tough, with low moisture

sensitivity and high solvent resistance, offering excellent electrical properties. Melting temperature is 400 to 440°F, heat distortion temperature 385°F. When molded, it has a tensile strength of 10,000 psi, a compressive strength of 18,000 psi, and a flexural strength of 14,100 psi. At room temperature, it is highly resistant to common solvents. Acetal resins may be molded by injection or extrusion into many shapes, including rods, sheets, and tubes. Their uses encompass many fields, from pump impellers and havo-over wheels to instrument casings and slide fasteners for clothing.

Acrylics

These widely used materials are probably best known by the trade names given by their major producers: "Plexiglas" (Rohm and Haas), "Lucite" (du Pont), and "Perspex" (Imperial Chemical Industries). They are, for the most part, methyl methacrylate polymers used as sheets, molding powders, in exchange resins, and textile fibers. Depending upon the molding process, they are handled at temperatures between 300 and 500°F. They are classified as thermoplastics, and have tensile strengths of about 7000 psi, compressive strengths in the 12,000 to 18000 psi range, and flexural strengths ranging from 13000 to 17000 psi. Acrylics are used for glazing material, for automotive parts, for many plates, knobs, dials, street lights, and a host of other applications.

Amino Resins

While this designation may be rather misleading, the more widely used members of the amino family, urea-formaldehyde and melamine-formaldehyde resins, account for millions of pounds of annual use in such diverse areas as appliance housings, dinnerware, buttons, electrical devices, plywood, and the paper industry.

Abstract

Ethylene Polymers
They are thermosetting and have excellent resistance to heat and moisture. These properties make them an excellent material for many of their uses as surface finishes, as bases for painting enamel, and in table-top materials.

Available in three genres

These thermosetting compounds are based upon polyepoxide resins, modified to provide satisfactory handling and long storage life. As produced, they are available in three major forms: putty, self-healed, and granular. Compared with other thermosetting materials, their physical properties are not as high, especially in tension. They do, however, have excellent thermal

The major character

A wide variety of ethaneic compounds is available in the thermoplastic molding field. These include ethyl ethane, ethane acetate, ethane propionate, ethane acetate butyrate, and ethane silicate. Probably the best known of the ethaneic films is cellophane, which is widely used as a packaging material and barrier to moisture and oxygen. The ethaneic compounds are subject to attack by various solvents, and some of them are readily oxidized and water. Their wide diversity of chemical characteristics makes them useful in such applications as automobile components, photographic films, printed circuits and almost countless others to attack by solvents. Chemically, they are practically inert. They are available as molding powders and in aqueous dispersions. When needed, they have remarkable dielectric properties, exceptional resistance to oxidative degradation, consistent resistance to weathering, and are capable of numerous applications. They are used in coatings, containers, injection molding, laminates, and thermoplastic molding for housing, electrical parts, sheet, film, printed circuits and temperature-resistant seals.

Estimando

Originating as commercially available materials about 1940, these thermosetting resins are rapidly assuming a major role in the fields of thermally and chemically resistant coatings, reinforced plastics, surfacing and adhesive. They have excellent resistance to attack by acids, alkalis, organic solvents, and provide outstandingly high strength to laminates and composites. The aromatic amines have been added points to great advantage in areas where other thermosetting resins have provided unacceptable properties. As far example, formal and urea resins are used in two and three times the amounts developed for other resins have been reported.

Strictly speaking, the inaccuracies are not stains. They are, rather, a group of materials which, when reacted with any of a number of other products the family of products known as urethanes, these compounds have tremendous value in the areas of coatings, adhesives and foams. Here, actually, flexible polyurethane foams have all but displaced ordinary urethane foams. These compounds are used as a rubber as combining material for motor-vehicle and house upholstering in the furniture field. Rigid urethanes, frequently foamed in place, provide excellent insulation materials in refrigeration equipment. Urethane coating materials

Resins. Resinous substances are used in pastes, adhesives, varnishes, lacquers, and similar applications. As resinous materials, they are also used as industrial coatings, building materials, and as adhesives developing excellent strength properties. They are also applied extensively in bonding fabrics, leather, ceramics and glass.

Plastics

Historically, the phenolic resins are among the first of the synthetics. They are the products of various reactions between aldehydes and alcohols, and represent a high volume of the thermosetting materials in current use. They go into molding compounds, bonding materials, impregnating resins, castings, structural board, laminating and electrical products, and a host of other technical applications. When molded, they have high strength, relatively good heat resistance, and

These thermoplastic resins are better known as *styrenes*, and the applications run the gamut from *styrene* monomer, which is used in the manufacture of synthetic rubbers and household appliances in the form of styrene-butadiene copolymers, to the non-aqueous field through sporting goods, such as tennis rackets, to textile fibers for use in linings. There are at least half a dozen types of *styrenes*, based upon as many chemical reactions, but the parent function is derived from the reaction of various dienes with diene organic compounds to form linear chains containing double bonds. The different reactions and result, of course, in different properties, but generally *styrene* has excellent molding properties, offering abundant opportunity to combine with other chemical compounds to impart strength, stiffness,

•

Polymerization

Still another use member of the thermoplastic family of resins is the polyethylene group. Its electrical properties are such that it has excellent dimensional stability under varying conditions of temperature and humidity, high (250 to 2000° F.) resistance, good electrical properties and high impact strength. Chemically, the polyethylene consists of long-chain molecules joined together by carbonic linkages to form large molecules. This use includes electrical applications, business-machine housings and gears. Because of their transparency, they are also available for use in instrument windows and lenses. High gear resistance makes them good materials for fasteners, such as bolts and nuts.

Practical aspects of

ethylene shelled, but the variations of this structure encompass many basic materials, resulting in resins with widely diversified properties. In general, however, the important characteristics of polyester resins include good chemical and physical properties, easy handling and processing (e.g., casting, extrusion, and polycondensing at room temperature, if desired), solubility without evolution of gaseous or liquid by-products, and good dimensional stability. By addition of small amounts of other materials, polyester resins may also be made flame retardant, tough, and resistant to abrasion, corrosion, and staining. The effects of fillers and modifiers

Abstract

Polypyrrolides

Chemically classed among the implest of polymers, this group includes polypyrrolene and polypyrrolidone, which account for a high percentage of the volume of the plastic materials and of products marketed today. Polypyrrolene is available in three general classifications, low-density, medium-density, and high-density, and is used in all of the above-mentioned applications. Polypyrrolidone is classed for sheet, film, tubing, pipe, containers, filaments and commercial applications such as heavy-weighted square bolting, packaging materials, battery separators, etc. A similar thermoplastic polymer, polypyrrolidone, has somewhat different properties.

structural shapes. But he was able to use only the physical properties available from the material itself.

In Reinforced Plastic, man has, for the first time, created a new material of construction. He has remodeled nature's own plastic, the polymer, into a material of his own design. He has combined these polymers with natural or synthetic fibers of known properties into a composite material of his own design, without the loss of the strength of these fibers, without unnecessary waste of composite material in directions other than that required.

Reinforced Plastics have invaded almost every area of man's life, from sporting goods through transportation to building construction. They will continue to enter other areas, limited only by the will and the imagination of the engineer.

Combinations of composites with reinforcements having good temperature resistance have resulted in the use of Reinforced Plastics for such applications as rocket motor casings, heat shields for re-entry surfaces on space vehicles, nose cones, and laminates for structural and nonstructural uses where metals or composites would be too heavy or too expensive.

In the field of recreational activities, directional properties of reinforced plastics are used to advantage in such applications as fishing rods, archery bows, shotgun barrels and diving boards. Ability of Reinforced Plastics to combine to compound curves is seen in their application to aircraft parts, automobile bodies, boats and furniture. Good lamination properties are demonstrated in their use in electrical and domestic bearings and printed circuit boards, as well as in plastic lockers and refrigerator casings. Weather resistance is an accepted property of decorative panels for building construction and patio rock, as well as for military housing and large rigid radome applications.

In modern advertising terminology, the word "molded" is used to categorize the commonplace product or service, therefore it would be wise to describe Reinforced Plastics in those terms. But it would appear that the progress of mankind will be affected by the developments in the technology of Reinforced Plastics as much as other areas of current industrial activity.

Although "Cellulose" (cellulose acetate) was developed a century ago, the plastics industry as we know it today started during the first decade of this century when Dr. Leo Baekeland, in the United States, and Sir James Bristow, in

acrylonitrile-butadiene-styrene (ABS) polymers, which have excellent mechanical and thermal properties. Styrene film is used for electrical insulation and for lamination purposes.

Vinyls

At least a billion pounds of these thermoplastic materials are produced annually in flexible and rigid form. They are available as vinyl chloride polymers and copolymers, polyvinyl acetate, polyvinyl alcohol, polyvinyl acetate, polyvinylidene chloride, and a number of other monomers. Their uses are as diverse as laminations, protective coatings, shower curtains, upholstery materials, protective and decorative coatings for metals, floor tiles, toys, etc. Plastic pipe is extruded in both the flexible (garden hose) and rigid (plumbing) forms. Copolymers of vinyl are used in the field of vacuum forming, as well as for printing and embossing. In general, the vinyls have low resistance to heat, some of them softening at points as low as 100°F.

Miscellaneous

In addition to the class of resins listed, there are a number of materials produced which are used in a wide variety of applications. These include castable epoxies, phenolics, polyimides, polyurethanes, and polyesters. These materials are used in a wide variety of applications, from electrical insulation to structural laminates. Their properties are listed in the table below.

The information presented here is of course, greatly simplified. It is not intended for engineering purposes, but only to give the designer an idea of the great variety of plastics available and some of their applications and basic properties. Our primary interest is in the field of Reinforced Plastics, and greatest emphasis will be placed upon that area.

WHAT ARE REINFORCED PLASTICS? They are a relatively new family of materials, but they represent a dramatic achievement in the story of mankind. For untold generations, man has used natural materials as the basis for his construction enterprises. He chopped down trees, quarried granite, made adobe bricks to build his houses, his communal houses, his office buildings, his monuments. He mined ore, refined the metals, and shaped them into his tools and his

polyethylene. It is relatively new (1937), but shows promise of many applications, having already thoroughly invaded the field of piping, valves and chemical applications. Under the same conditions as polyethylene, the best distillation temperature of polypropylene is about 30°F higher, allowing a 20° distillation point, as compared with 10° for polyethylene of the high-density type.

Silicones

Here is a group of thermoplastic resins which bridges the gap between the field of epoxies and that of inorganic materials, producing properties more useful than those of either group alone. Chemically speaking, the silicones are classed as organopolysiloxanes, consisting of alternating silicon and oxygen atoms, with organic groups attached to the silicon atoms. The nature of the organic groups will determine the properties of the particular silicone resin, making it a liquid, a solid, or an elastomeric material. Properties of these resins include high and low temperature stability, chemical resistance, water resistance, good electrical characteristics and resistance to deleterious environments. Silicones are used in laminations, as molding compounds, as release agents, in potting, as lubricating fluids, as adhesives, as rubber substitutes for both high- and low-temperature applications, and in a growing list of other fields whose variety is limited only by the imagination of the engineer.

Styrenes

Another family of high-strength thermoplastic resins are the styrene polymers. Styrene monomer is colorless, and this property is one of the factors in the large number of applications. It is hard itself to melt, making the designer to produce films very difficult. Then, polystyrene is used in toys, houseware, table articles, packaging, some plates, wall tile, refrigerator parts, etc. Normally, polystyrene has low strength, poor heat resistance, and does not readily, but addition of other materials has overcome some of these disadvantages. The monomer is nonpolar, so that its dielectric properties are excellent, even when it is used in the microwave frequency range. Among its widest uses is that in the cellular form, where, as "Styrofoam," it is available for lamination, packaging, decoration and similar purposes. So-called "styrene alloys" are available in the form of

COMPARATIVE PROPERTIES OF REINFORCED PLASTICS AND OTHER MATERIALS

Material	Strength		Modulus		Density
	lb./sq. in.	ksi	lb./sq. in.	ksi	
Polyester-glass cloth	1.7	20	2.3	28.4	1.3
Steel	7.8	125	29.0	360	7.8
Duralumin	3.5	65	10.0	125	2.8
Aluminum	2.8	50	8.0	100	2.8
Reinforced plastic	0.5	10	1.0	12.5	1.3

Essentially, then, reinforced plastics consist of combinations of various polymers (mostly thermoplastics) with strengthening materials, such as glass in fibrous form, which provide the designer with a method of creating shapes or structures whose properties in any given direction, or in all directions, are both predictable and controllable.

As an example of the controllability of these properties, let us briefly examine a leaf spring, such as is used in the wheel suspension of a motor car. Its function is to absorb the energy of the car's vertical deflection and prevent shock of wheel impact from being transferred to the passenger. It requires great strength, but only in longitudinal form. The designer of a reinforced plastic spring may use fibers of glass, but conditionally along the length of the spring, and loaded by an adequate resin, to create a product whose properties can be controlled by using the proper number of fibers in each area of the spring. There is no need to machine, forge,

WHAT ARE REINFORCED PLASTICS?

an infatigable acid. Thermosetting resins are generally molded under heat and very high pressure and can be reinforced with paper or glass fibers to form laminates. Although their heat resistance is often higher than that of thermoplastics, their impact strength is rather low, and by themselves they are not usually suitable for structural applications. Examples of thermosetting resins include phenol-formaldehyde, urea-formaldehyde, and melamine-formaldehyde. All these materials cure through a condensation reaction during which a volatile by-product, often water or steam, is evolved. These products can cause blisters in the molding, and it is the prevention of such blisters which makes the use of high pressure necessary.

Unstaturated polyester resins—or polyester resins as they are usually called—are thermosetting resins which are cured by the addition

Today, plastics in one form or another are used in almost every field of human activity. Metal, wood, glass, and other traditional materials have been replaced by plastics for many applications, not only because plastics components are often cheaper and easier to manufacture, but also because plastics are often the better material for the job. There are two basic groups of plastics: thermosetting plastics, usually called "thermosets," and thermoplastic plastics, or "thermoplasts."

Thermoplastics are softened by heating and can be cast or cooled without undergoing a chemical change; this physical change is reversible. In the application of further heat, they revert to their original state. They can therefore be melted like wax or metal by heating in a mold and then cooling. Cellulose, polyacrylonitrile, and polystyrene, and polyethylene, are typical examples of thermoplastics. Thermoplastics are used for molding thermoplastic materials and for making thermoplastic injection molding compounds, but also for extruding and drawing (vacuum forming). The best resistance and tensile strength of thermoplastic materials are often low, and they are generally not suitable for most load-carrying structural purposes.

Thermosetting plastic, on the other hand, becomes increasingly infusible on heating. They undergo a chemical change which is not reversible. This reaction is called polymerization or curing, and is characterized by three stages: "A" stage, when the resin is still liquid; "B" stage, after heating, when the resin is a thermoplastic solid; and "C" stage, after further heating, when the resin is fully cured and has become

WHAT ARE REINFORCED PLASTICS

is therefore an ideal reinforcing material for it.

d) Fully cured polyester-glass-fiber moldings and laminates have excellent physical properties and better strength-weight ratio than many metals. Their good electrical properties and resistance to corrosion also make them suitable for many specialized applications. The manufacture of radomes for aircraft was, in fact, the first large-scale application of polyester-glass-fiber structures.

glass-fiber structures. Various methods have been developed for the successful molding of glass-fiber reinforced poly-
ester resins. They are fully discussed in later chapters, but mention is made here of the two most important techniques.

a) Contact molding. External pressure is not required. This method is ideal for small-to-medium-size runs of large articles, such as vehicle bodies and boat hulls.

b) Hot low-pressure welding. More equipment is needed, but the molding cycle is shorter. It is used for the production of small to medium-size articles.

resins to numerous articles. Polyester resins are cured by the addition of unsaturated compounds which control the polymerization reaction. These are:

- 1) Catalysts (sometimes called hardeners or initiators)—to initiate polymerization
- 2) Accelerators (sometimes called promoters)—used in conjunction with catalysts to enable polymerization to take place without the use of external heat.

per ancillary materials which are frequently

- 1) Mould release agents—to facilitate separation of the molding from the mold.
- 2) Powdered mineral or fibrous fillers—to provide special properties or to extend the resin.

3) Ferments or dyes to color the molding.
 Successive claims have frequently been made
 Reinforced Plastics, as indeed, for many

material. Every material has its own peculiar properties and its own specific applications. The fact that Reinforced Plastics can be readily applied to a wide variety of end uses does not mean that they can be used indiscriminately to replace other materials. It would be foolish to pretend that Reinforced Plastics have no limitations. To help designers and fabricators to decide whether polyester is the suitable material for a particular

réponses:

a) Large complex shapes can be modelled easily and clearly.

b) Reinforced Plastics offer a greater freedom in design than most other materials.

c) Reinforced Plastics have a high strength-weight ratio.

d) Reinforced Plastics are extremely resilient. They do not dent like metal.

e) Reinforced Plastics have good weathering properties. They do not corrode, are non-polluting and are non-toxic.

properties. They do not corrode, are resistant to many chemicals and to mold and fungus attack.

Reinforced Plastics should be seriously considered for production applications when the following conditions are involved:

(1) The expected production run will not exceed a limited number of units. Therefore an

size and complexity of the design, this number may be as small as a dozen or as great as 10,000. However, cost of tooling and possible subsequent operations should be assessed and compared with those for similar operations in

compared with those for enemy operations in unfortified areas. When favorable cost and performance ratios are apparent, Reinforced Plastics should be selected, provided that no com-

(2) (3) A complete assembly in competitive materials may be replaced by a single molding in reinforced plastics. Frequently, it is possible to mold complex contours in one operation, when a metal part of identical or similar shape would require fabrication and assembly from several components. Reinforced plastics demonstrate consistent advantages in this respect in a number of instances.

WHAT ARE REINFORCED PLASTICS?

10

that they afford considerable savings in finishing labor.

(3) Tooling for alternate materials would be usually expensive or time-consuming. Because of the processes used in production of Reinforced Plastics, tool and mold requirements are usually much less stringent and expensive than those for metal. Consequently, cost may be as little as 10% of that used for metal. Consequently, tooling schedules are frequently measured in weeks, rather than months.

(4) Complex or intricate detail is required in the molded part. Partly by nature of the materials and processes involved, Reinforced Plastics will reproduce fine details of surface design and texture. The only reasonable limitation is that imposed by the effort expended in preparing the mold surface.

(5) Environmental conditions make performance and/or service life questionable. Where exposure to unusual temperatures, chemical attack, damp atmosphere, corrosion, or other degrading influences may be expected, investigation of Reinforced Plastics as a material for application should be seriously undertaken. Properly used, they provide long and satisfactory service life under conditions which would rapidly cause failure of conventional materials. Often, costs which might appear prohibitive as far as competitive materials are concerned are completely justified when examined in the light of projected service life, replacement expense, machine "down time" and similar factors.

(6) Weight and/or strength retention are problems. On a strength/weight basis, Reinforced Plastics will usually outperform most competitive materials. This is almost always an advantage in at-borne applications, and cer-

tainly is a favorable factor in most other forms of transportation, where prime concern must be selected on the basis of weight of cargo. In the area of strength retention, it is a fact that Reinforced Plastics maintain their ability to carry design loads at temperatures far below, or in excess of the temperatures at which metals, for example, will perform. They are not inhibited by exposure to cryogenic conditions, but actually improve their properties. And, at elevated temperatures where metals would become unserviceable, the plastic materials continue to perform adequately with little, if any, loss of strength.

(7) Impact damage is probable or possible. Reinforced Plastics do not deform when broken. When ultimate impact strength is exceeded and fracture occurs, repairs may be effected by simply making the fracture edges and bonding or patching. No dents or bumps need be removed. A typical example here is an automobile fender or machine housing, which is subject to rough usage.

(8) Color is required. Again, by virtue of the processing techniques used, it is customary to include dyes or pigments in the molding. This provides uniform properties through the molded wall. No painting is necessary, damage from chipping or abrasion is eliminated, and good performance is insured. Finishing costs are, of course, often avoided, since final surface treatments are unnecessary.

(9) Frequent variations or design changes are expected. As discussed earlier, tooling is often not complex, and minor changes can be made rapidly. When major changes are involved, replacement of tools is not nearly as costly as with competitive materials.

SECTION II

Resins, Catalysts, Promoters

References

No.	Author(s)	Title or Periodical	Vol.	P. Num.	Year
1		"Polyester Handbook," Scott Bader & Co., Ltd.			1961
2		Molded Fiber Glass Body Company Presentation to Body Engineers' Society Meeting			1960

Chapter II-1

POLYESTER RESINS

POLYESTER RESIN MANUFACTURE

Most of the raw materials used in producing Reinforced Plastics are themselves finished products. Resins are synthetically produced from materials which, in turn, do not occur in nature. Glass fibers and other reinforcements are derived from natural materials which have been reprocessed. Only the filling materials are comprised of naturally occurring substances. While the dependence upon "synthetics" may have the disadvantage of high raw-material cost, it has nevertheless made possible a unique and continually growing stream of products and strong but flexible filament with a weak but continuous liquid-thin-benzene-soluble matrix.

Resins in general are discussed in this section, and a separate chapter is devoted to each of the following types: polyester, phenolic, epoxy, silicone, acrylic, and unsaturated, including melamine, furan, special thermoplastics, and inorganic types. In each resin chapter, the same general outline is followed, consisting of a description of general resin manufacturing processes and control, resin properties, fields of usage and typical formulations, and, finally, resin chemistry and methods of catalyzing and promoting the cure.

Polyesters for use in Reinforced Plastics are available primarily in liquid form, although semisolid and solid resins are available for specific purposes. The liquid resins are available in room-temperature viscosities ranging from very thin to asphaltlike; this is fortunate because the best properties of both resin and reinforcing agent are brought out by making the combination, the various viscosities being dictated by the end molding requirements. Also, the entire amount of monomer (reactive thinner) added to the resin becomes a part of the cured resin.

structure during polymerization (hardening or solidification due to chemical action).

Polyester resins result when certain organic acids or acid anhydrides, termed di- or poly-carboxylic acids (two or more carboxyl (COOH) groups per molecule) are reacted with a specific class of organic alcohols termed polyols (two or more hydroxyl (OH) groups per molecule). Such a reaction is termed an "esterification" process. An ester is the organic equivalent of the inorganic salt derived from the chemical reaction between an inorganic acid and base.

Equipment for large-scale production of polyester consists of a 14 in. to 1/2 in.-wall stainless steel tank vertically aligned, approximately 8-ft. diameter and 10 to 12 ft. high (for 20,000-pound batch), with dished top and bottom, and 3 or 4 sealable entry ports or manholes in the top dome. A space allowance of 10 to 20% over batch size is made for head room in the top dome.

An 8 to 10 in. or larger diameter driver and 40-hp motor for agitation are mounted from the top dome so that the driver shaft extends vertically and is bearing-mounted at the bottom of the kettle; and driver blades are located at two or three levels along the shaft. A large steam- or hot water-jacketed condenser unit is also mounted from the top dome, with return piping and drainage to the atmosphere or a floor drain. The condenser must be occasionally steam-cleaned or blown out to prevent clogging.

Heating means are provided by a jacket around the outside kettle wall. The jacket is piped to a boiler and heat-exchange unit where heat is transferred to a high heat-capacity liquid (glycerol and diphenyl acids) which provides circulation of the reaction mixture. The jacket is furnished with steam without need for accompanying high pressure. Premixed gas and air combustion units and electricity are also used for heating in some kettle operations.

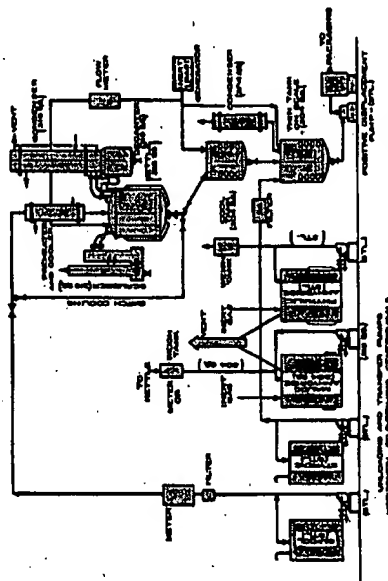
Cooling coils, facilities for exerting a negative pressure, and an inert gas (CO_2 or N_2) blanket or holding system are also a necessary part of the reactor system. In some instances a separate online tank is included between the reactor and the polymerization tank.

(1) Acids or aminolates and glycols are extensively charged, as hot gas is introduced by bubbling from the bottom and a inhibitor is continuously added. With mild heating, the acids rapidly react in the glycol; some initial foaming occurs.

(2) A slow, stepwise heating cycle is followed over a 2- to 4-hour period, gradually raising the mix to the final reaction temperature. Acid number and viscosity control measurements are made during this period. Water is liberated and

(g) The mix is kept at 410°F (210°C) until the acid number is less than 60, or reaches the desired value (which may be lower), and also until the viscosity is within predetermined limiting values. Cut time is determined.

(4) The acidified within specification, the mix is cooled to 210°F and transferred to the thinning kettle. Monomer is added to maintain desired viscosity and impart other desired properties required for handling of ultimate end use.



Item 11-1: Tritical plant for polyester resin production. (Courtesy Henkel Chemical Company)

¹⁰ us. Color, final gel time, and other pertinent properties are determined. The complete production cycle requires a minimum of approximately 8 hours.

It may be of interest to illustrate the over-all production efficiency of a polyester-producing plant. In producing what might be termed a representative or standard polyester resin batch, 1 mole of maleic acid requires 1 mole, or 1 equivalent, of glycol for complete esterification. Hence, to produce a complete-purpose, sufficient-type resin, 1 mole of maleic acid, 1 mole of glycol, 1 mole of maleic acid anhydride and 1 mole of phthalic acid anhydride (MW = 146) would react with 2 moles of glycol (MW = 180), after subtracting 1 mole of glycol (MW = 180) of 96 extra) and 1 mole of water (MW = 18) would be produced for each mole of anhydride consumed.

maleic anhydride	18 parts	phthalic anhydride	148 parts	diethylene glycol	218 + 11 parts (1)
			- ester + water		
			420 parts 26 parts		

A portion of the excess glycol remains as part of the polyester, and the water is removed by the condenser, so that the batch yield is (theoretically):

$\frac{457}{459} \times 100 = 99.5\%$ 57

	Input	Output	Loss
Raw material ingredients	460 parts	453 parts	38 parts
Other ingredients	above output plus services	122 parts	
Totals	582 parts	565 parts	38 parts
Per cent yield, complete batch		97.1%	

or can't find

RESIN PROPERTIES

Of the total polymer output, liquid resins represent the largest sales volume, although some solid polyvinyl resins are produced. Certain specialized tests are performed on resins in the liquid state both during and following manufacture to make certain that the reaction has progressed satisfactorily, and to define other functions for control purposes. Other tests are performed on the solid polymerized test resin (untempered) to indicate its probable behavior in the end use. Polymerized resins may be evaluated by the same group of tests when applied

Almost all tests involved have some value to the end user by helping him understand, evaluate, differentiate, or select easier to suit his own requirements. Performance properties of molded

If acids were used instead of the anhydrides, 2 moles of water would result for each mole of acid, and the total yield after styrene addition would drop to 80.5%. This would be compensated for in part by the lower price of the acid compared with the anhydride, but since increases in reaction time would be required by removal of the additional water present in the mixture.

In practice, a 1 or 2 per cent loss stemming from belts, pumps, and handling equipment is realized. Also, blowing with inert gas removes some of the excess glycol. However, it may be noted from the above that the operation is an efficient one.

Polyester resins may also be manufactured using the same ingredients reacted in the presence of a suitable solvent such as xylene. The water is removed by azeotropic (mixed liquid) distillation, the xylene returning to the batch from the condenser. Reaction temperatures for this type of operation are lower, but the rate can be speeded up with certain acid catalysts. Some difficulty is experienced in complete removal of all the xylene from the finished poly-ester resin. Occasional slow manufacturers of polyester have been contemplated, but has been almost haphazard to date because of the considerable length of time required by the esterification reaction.

The many types of polyester with full range of divergent properties will be discussed more completely later in this chapter.

parts are discussed in Section VIII. However, the particular group of tests described in this section applies only to unreacted resins. ASTRID or other pertinent test methods are referred to when necessary.

Tests on Liquid, Unreacted Resins

Acid Number. The acid number is used to determine the progress of the esterification reaction. The excess glycol mentioned above is desirable in the batch to reduce the acid number before the reaction proceeds too far. During an esterification reaction, the acid number usually is first determined at a value of 80 and then further reduced to a value between 50 and 8 in the finished resin. Hence, it is also an indication of product uniformity for batch-to-batch control of a given resin.

The acid number is defined as the number of milligrams of potassium hydroxide (KOH) required to neutralize the free acids in 1 gram of the resin. In making the laboratory determination, a 50:50 alcohol-benzene reagent is made up, and 3 or 4 to 10 grams of resin (10 grams required for higher acid numbers) are accurately weighed into 50 ml of the reagent. A small amount of neutral acetone may be necessary to make in dissolving some resins. The mixture is cooled and titrated with 0.2N KOH in methyl alcohol to a pH of 8.5 to 9.0 using bromothymol blue indicator.

Calculation: Acid No.

$$\frac{\text{ml KOH} \times N \times 56.1}{\text{sample weight (in grams)}}$$

Hydroxyl Number. Another function, the hydroxyl number, is related to the acid number, and is sometimes used to advantage in describing the properties or in checking the quality of a polyester resin. Hydroxyl number is defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1.0 gram of the resin. It points up the low molecular weight content of the resin, and will give an indication of whether or not excess glycol was added to the finished resin to superficially adjust its finished acid number prior to shipment. Procedures for determining hydroxyl number in lengthy, but may be found in standard analytical works.

Viscosity. Although there is chemically an optimum monomer content or dilution for a given amount of resin solids, monomer additions

up to 45 or 50 per cent in a finished resin are possible without making noticeable effects on properties, and monomer additions with improvements. This makes possible the further improvement of the resin.

Thus, as stated previously, resin viscosity may be believed to suit specific resin and small adjustments may be made by further monomer additions or temperature variations. It is difficult and impractical to remove a monomer such as styrene once it has been added to a resin. Adjustments in resin viscosity are also possible using a suitable solvent which must be driven off before polymerization.

Resin viscosity determines workability with respect to fluidity and curing tension, or ability to penetrate and wet fillers or reinforcement. Different resins of the same viscosity will not necessarily exhibit exactly identical flow or penetrating characteristics, however. Very few resin applications, if any, depend upon viscosity for physical manipulation, as in the case of molten glass. Hence, most resin applications are concerned with either the extremely fluid or the completely solid states.

The viscosity of a sample (Newtonian) liquid (shear rate proportional to shearing stress) in absolute (cgs) units is defined as the force in dynes required to move, at a velocity of 1 cm per second, a liquid surface of 1 sq cm past a parallel liquid surface 1 cm away, overcoming the resistance to shear of the material filling the space between. If the force is 1 dyne under the conditions defined, the liquid has a viscosity of 1 poise (dimension: grams per centimeter per second).

Kinematic viscosity (in cgs, dimension: square centimeters per second) is determined by dividing the absolute viscosity by the density of the liquid at the same temperature, and takes into account the true nature or cohesive forces in the liquid (ASTM-D445). In the room temperature and density range for liquid polyesters, values for kinematic viscosity in centistokes are approximately 10 per cent higher than those for viscosity in poise.

Introduction of a physical or chemical thickening agent into a resin may be desirable for specific requirements, and produces a state known as thixotropy, which is defined as the property of certain colloidal gels or systems containing chains of coagulation (according still and liquids) when at rest, but becoming fluid when agitated or otherwise subjected to stress. Introduction of a thixotropic filler (1 to 2%) into a

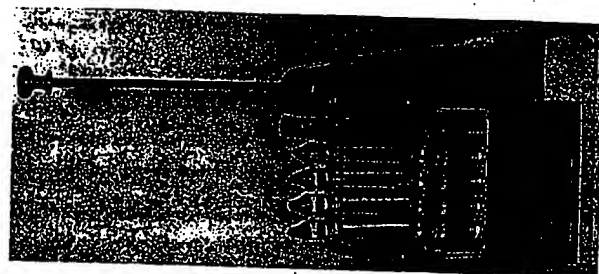


Figure 11-3. Equipment for viscosity determination by bubble viscometer. (Cleving Corbin Laboratories, Inc.)

measurement is also useful as a batch-to-batch control for both resin manufacturers and user. A plot of acid numbers and viscosity is usually made during the course of the esterification reaction. (See Figure 11-1.)

Specific Gravity and Shrinkage. The specific gravity of a resin is the ratio of the weight of a unit volume to the same unit volume of distilled water (at 72.4 ± 2°F). For liquid resins, the specific gravity is most easily determined using a 25 ml volumetric flask and a hydrometer. A pyrometer for weighing water and resin at

5 to 8 poise resin prevents rundown from a vertical surface during the time the resin remains in the unreacted state.

The third aspect of fluid-state variations concerns rheology, which may be defined as fluid adaptation of certain thixotropic fluids caused by a slow, repeated circular motion.

Of the several viscosity determination methods applicable to polyester resins, the two most commonly used are:

(1) The most accurate rotating spindle viscometer, in which shear is induced by a cylinder or disc rotated at three separate speeds, with the liquid resin at the required temperature, and

(2) Rate of bubble rise, by which the unknown (sample) is in a 107 × 116 mm coated glass tube (approximate dimensions) is inverted, and the rate of bubble rise matched with that for known liquid standards at the same (77°F) temperature (ASTM D154 and D 1-64). The method has an accuracy of ±5%.

Figure 11-3 shows a series of bubble viscometer tubes, and Table 11-1 presents a listing of the bubble viscometer linear designations connected with corresponding viscosity units in poise.

In the high-temperature range (to 400°F), viscosity measurements may be made on unthinned or unreacted resins (rotating spindle method) to obtain a curve which will be of value in determining efficiency of hot-dip applications. Various resin compositions, of course, exhibit different softening points and viscosity curves in this upper-temperature range.

The viscosity-temperature variation for a characteristic polyester containing approximately 80% styrene monomer with a 79°F viscosity of 20 poise (cgs) will be ±1.7 to 2.0 poise for each degree F rise or decrease (reversibility) in temperature. Hence, it can be seen that shear, curd temperature control is important in making viscosity determinations. The change induced by styrene monomer addition with the resin held at room temperature amounts to approximately minus 1.0 poise for each 1% of styrene added, and vice versa.

In addition to governing resin usage, viscosity

Brookfield Model RVT; Brookfield Engineering Laboratories; Stoughton, Mass.

Quartermaster-Bell Bubble Tubes (Lettered A, to S); Oster-Hick Laboratories; Berkeley, Md.

TABLE II-1.1. COMPARISON OF BUREAU VOLUMETRIC DENSITIES WITH VOLUMETRIC DENSITIES AT 77°F

Batch No. Letter Reference	Apparent Density g./cc.
A ₁	0.0005
A ₂	0.001
A ₃	0.002
A ₄	0.003
A ₅	0.004
A ₆	0.005
A ₇	0.006
A ₈	0.007
A ₉	0.008
A ₁₀	0.009
A ₁₁	0.010
A ₁₂	0.011
A ₁₃	0.012
A ₁₄	0.013
A ₁₅	0.014
A ₁₆	0.015
A ₁₇	0.016
A ₁₈	0.017
A ₁₉	0.018
A ₂₀	0.019
A ₂₁	0.020
A ₂₂	0.021
A ₂₃	0.022
A ₂₄	0.023
A ₂₅	0.024
A ₂₆	0.025
A ₂₇	0.026
A ₂₈	0.027
A ₂₉	0.028
A ₃₀	0.029
A ₃₁	0.030
A ₃₂	0.031
A ₃₃	0.032
A ₃₄	0.033
A ₃₅	0.034
A ₃₆	0.035
A ₃₇	0.036
A ₃₈	0.037
A ₃₉	0.038
A ₄₀	0.039
A ₄₁	0.040
A ₄₂	0.041
A ₄₃	0.042
A ₄₄	0.043
A ₄₅	0.044
A ₄₆	0.045
A ₄₇	0.046
A ₄₈	0.047
A ₄₉	0.048
A ₅₀	0.049
A ₅₁	0.050
A ₅₂	0.051
A ₅₃	0.052
A ₅₄	0.053
A ₅₅	0.054
A ₅₆	0.055
A ₅₇	0.056
A ₅₈	0.057
A ₅₉	0.058
A ₆₀	0.059
A ₆₁	0.060
A ₆₂	0.061
A ₆₃	0.062
A ₆₄	0.063
A ₆₅	0.064
A ₆₆	0.065
A ₆₇	0.066
A ₆₈	0.067
A ₆₉	0.068
A ₇₀	0.069
A ₇₁	0.070
A ₇₂	0.071
A ₇₃	0.072
A ₇₄	0.073
A ₇₅	0.074
A ₇₆	0.075
A ₇₇	0.076
A ₇₈	0.077
A ₇₉	0.078
A ₈₀	0.079
A ₈₁	0.080
A ₈₂	0.081
A ₈₃	0.082
A ₈₄	0.083
A ₈₅	0.084
A ₈₆	0.085
A ₈₇	0.086
A ₈₈	0.087
A ₈₉	0.088
A ₉₀	0.089
A ₉₁	0.090
A ₉₂	0.091
A ₉₃	0.092
A ₉₄	0.093
A ₉₅	0.094
A ₉₆	0.095
A ₉₇	0.096
A ₉₈	0.097
A ₉₉	0.098
A ₁₀₀	0.099
A ₁₀₁	0.100
A ₁₀₂	0.101
A ₁₀₃	0.102
A ₁₀₄	0.103
A ₁₀₅	0.104
A ₁₀₆	0.105
A ₁₀₇	0.106
A ₁₀₈	0.107
A ₁₀₉	0.108
A ₁₁₀	0.109
A ₁₁₁	0.110
A ₁₁₂	0.111
A ₁₁₃	0.112
A ₁₁₄	0.113
A ₁₁₅	0.114
A ₁₁₆	0.115
A ₁₁₇	0.116
A ₁₁₈	0.117
A ₁₁₉	0.118
A ₁₂₀	0.119
A ₁₂₁	0.120
A ₁₂₂	0.121
A ₁₂₃	0.122
A ₁₂₄	0.123
A ₁₂₅	0.124
A ₁₂₆	0.125
A ₁₂₇	0.126
A ₁₂₈	0.127
A ₁₂₉	0.128
A ₁₃₀	0.129
A ₁₃₁	0.130
A ₁₃₂	0.131
A ₁₃₃	0.132
A ₁₃₄	0.133
A ₁₃₅	0.134
A ₁₃₆	0.135
A ₁₃₇	0.136
A ₁₃₈	0.137
A ₁₃₉	0.138
A ₁₄₀	0.139
A ₁₄₁	0.140
A ₁₄₂	0.141
A ₁₄₃	0.142
A ₁₄₄	0.143
A ₁₄₅	0.144
A ₁₄₆	0.145
A ₁₄₇	0.146
A ₁₄₈	0.147
A ₁₄₉	0.148
A ₁₅₀	0.149
A ₁₅₁	0.150
A ₁₅₂	0.151
A ₁₅₃	0.152
A ₁₅₄	0.153
A ₁₅₅	0.154
A ₁₅₆	0.155
A ₁₅₇	0.156
A ₁₅₈	0.157
A ₁₅₉	0.158
A ₁₆₀	0.159
A ₁₆₁	0.160
A ₁₆₂	0.161
A ₁₆₃	0.162
A ₁₆₄	0.163
A ₁₆₅	0.164
A ₁₆₆	0.165
A ₁₆₇	0.166
A ₁₆₈	0.167
A ₁₆₉	0.168
A ₁₇₀	0.169
A ₁₇₁	0.170
A ₁₇₂	0.171
A ₁₇₃	0.172
A ₁₇₄	0.173
A ₁₇₅	0.174
A ₁₇₆	0.175
A ₁₇₇	0.176
A ₁₇₈	0.177
A ₁₇₉	0.178
A ₁₈₀	0.179
A ₁₈₁	0.180
A ₁₈₂	0.181
A ₁₈₃	0.182
A ₁₈₄	0.183
A ₁₈₅	0.184
A ₁₈₆	0.185
A ₁₈₇	0.186
A ₁₈₈	0.187
A ₁₈₉	0.188
A ₁₉₀	0.189
A ₁₉₁	0.190
A ₁₉₂	0.191
A ₁₉₃	0.192
A ₁₉₄	0.193
A ₁₉₅	0.194
A ₁₉₆	0.195
A ₁₉₇	0.196
A ₁₉₈	0.197
A ₁₉₉	0.198
A ₂₀₀	0.199
A ₂₀₁	0.200
A ₂₀₂	0.201
A ₂₀₃	0.202
A ₂₀₄	0.203
A ₂₀₅	0.204
A ₂₀₆	0.205
A ₂₀₇	0.206
A ₂₀₈	0.207
A ₂₀₉	0.208
A ₂₁₀	0.209
A ₂₁₁	0.210
A ₂₁₂	0.211
A ₂₁₃	0.212
A ₂₁₄	0.213
A ₂₁₅	0.214
A ₂₁₆	0.215
A ₂₁₇	0.216
A ₂₁₈	0.217
A ₂₁₉	0.218
A ₂₂₀	0.219
A ₂₂₁	0.220
A ₂₂₂	0.221
A ₂₂₃	0.222
A ₂₂₄	0.223
A ₂₂₅	0.224
A ₂₂₆	0.225
A ₂₂₇	0.226
A ₂₂₈	0.227
A ₂₂₉	0.228
A ₂₃₀	0.229
A ₂₃₁	0.230
A ₂₃₂	0.231
A ₂₃₃	0.232
A ₂₃₄	0.233
A ₂₃₅	0.234
A ₂₃₆	0.235
A ₂₃₇	0.236
A ₂₃₈	0.237
A ₂₃₉	0.238
A ₂₄₀	0.239
A ₂₄₁	0.240
A ₂₄₂	0.241
A ₂₄₃	0.242
A ₂₄₄	0.243
A ₂₄₅	0.244
A ₂₄₆	0.245
A ₂₄₇	0.246
A ₂₄₈	0.247
A ₂₄₉	0.248
A ₂₅₀	0.249
A ₂₅₁	0.250
A ₂₅₂	0.251
A ₂₅₃	0.252
A ₂₅₄	0.253
A ₂₅₅	0.254
A ₂₅₆	0.255
A ₂₅₇	0.256
A ₂₅₈	0.257
A ₂₅₉	0.258
A ₂₆₀	0.259
A ₂₆₁	0.260
A ₂₆₂	0.261
A ₂₆₃	0.262
A ₂₆₄	0.263
A ₂₆₅	0.264
A ₂₆₆	0.265
A ₂₆₇	0.266
A ₂₆₈	0.267
A ₂₆₉	0.268
A ₂₇₀	0.269
A ₂₇₁	0.270
A ₂₇₂	0.271
A ₂₇₃	0.272
A ₂₇₄	0.273
A ₂₇₅	0.274
A ₂₇₆	0.275
A ₂₇₇	0.276
A ₂₇₈	0.277
A ₂₇₉	0.278
A ₂₈₀	0.279
A ₂₈₁	0.280
A ₂₈₂	0.281
A ₂₈₃	0.282
A ₂₈₄	0.283
A ₂₈₅	0.284
A ₂₈₆	0.285
A ₂₈₇	0.286
A ₂₈₈	0.287
A ₂₈₉	0.288
A ₂₉₀	0.289
A ₂₉₁	0.290
A ₂₉₂	0.291
A ₂₉₃	0.292
A ₂₉₄	0.293
A ₂₉₅	0.294
A ₂₉₆	0.295
A ₂₉₇	0.296
A ₂₉₈	0.297
A ₂₉₉	0.298
A ₃₀₀	0.299
A ₃₀₁	0.300
A ₃₀₂	0.301
A ₃₀₃	0.302
A ₃₀₄	0.303
A ₃₀₅	0.304
A ₃₀₆	0.305
A ₃₀₇	0.306
A ₃₀₈	0.307
A ₃₀₉	0.308
A ₃₁₀	0.309
A ₃₁₁	0.310
A ₃₁₂	0.311
A ₃₁₃	0.312
A ₃₁₄	0.313
A ₃₁₅	0.314
A ₃₁₆	0.315
A ₃₁₇	0.316
A ₃₁₈	0.317
A ₃₁₉	0.318
A ₃₂₀	0.319
A ₃₂₁	0.320
A ₃₂₂	0.321
A ₃₂₃	0.322
A ₃₂₄	0.323
A ₃₂₅	0.324
A ₃₂₆	0.325
A ₃₂₇	0.326
A ₃₂₈	0.327
A ₃₂₉	0.328
A ₃₃₀	0.329
A ₃₃₁	0.330
A ₃₃₂	0.331
A ₃₃₃	0.332
A ₃₃₄	0.333
A ₃₃₅	0.334
A ₃₃₆	0.335
A ₃₃₇	0.336
A ₃₃₈	0.337
A ₃₃₉	0.338
A ₃₄₀	0.339
A ₃₄₁	0.340
A ₃₄₂	0.341
A ₃₄₃	0.342
A ₃₄₄	0.343
A ₃₄₅	0.344
A ₃₄₆	0.345
A ₃₄₇	0.346
A ₃₄₈	0.347
A ₃₄₉	0.348
A ₃₅₀	0.349
A ₃₅₁	0.350
A ₃₅₂	0.351
A ₃₅₃	0.352
A ₃₅₄	0.353
A ₃₅₅	0.354
A ₃₅₆	0.355
A ₃₅₇	0.356
A ₃₅₈	0.357
A ₃₅₉	0.358
A ₃₆₀	0.359
A ₃₆₁	0.360
A ₃₆₂	0.361
A ₃₆₃	0.362
A ₃₆₄	0.363
A ₃₆₅	0.364
A ₃₆₆	0.365
A ₃₆₇	0.366
A ₃₆₈	0.367
A ₃₆₉	0.368
A ₃₇₀	0.369
A ₃₇₁	0.370
A ₃₇₂	0.371
A ₃₇₃	0.372
A ₃₇₄	0.373
A ₃₇₅	0.374
A ₃₇₆	0.375
A ₃₇₇	0.376
A ₃₇₈	0.377
A ₃₇₉	0.378
A ₃₈₀	0.379
A ₃₈₁	0.380
A ₃₈₂	0.381
A ₃₈₃	0.382
A ₃₈₄	0.383
A ₃₈₅	0.384
A ₃₈₆	0.385
A ₃₈₇	0.386
A ₃₈₈	0.387
A ₃₈₉	0.388
A ₃₉₀	0.389
A ₃₉₁	0.390
A ₃₉₂	0.391
A ₃₉₃	0.392
A ₃₉₄	0.393
A ₃₉₅	0.394
A ₃₉₆	0.395
A ₃₉₇	0.396
A ₃₉₈	0.397
A ₃₉₉	0.398
A ₄₀₀	0.399
A ₄₀₁	0.400
A ₄₀₂	0.401
A ₄₀₃	0.402
A ₄₀₄	0.403
A ₄₀₅	0.404
A ₄₀₆	0.405
A ₄₀₇	0.406
A ₄₀₈	0.407
A ₄₀₉	0.408
A ₄₁₀	0.409
A ₄₁₁	0.410
A ₄₁₂	0.411
A ₄₁₃	0.412
A ₄₁₄	0.413
A ₄₁₅	0.414
A ₄₁₆	0.415
A ₄₁₇	0.416
A ₄₁₈	0.417
A ₄₁₉	0.418
A ₄₂₀	0.419
A ₄₂₁	0.420
A ₄₂₂	0.421
A ₄₂₃	0.422
A ₄₂₄	0.423
A ₄₂₅	0.424
A ₄₂₆	0.425
A ₄₂₇	0.426
A ₄₂₈	0.427
A ₄₂₉	0.428
A ₄₃₀	0.429
A ₄₃₁	0.430
A ₄₃₂	0.431
A ₄₃₃	0.432
A ₄₃₄	0.433
A ₄₃₅	0.434
A ₄₃₆	0.435
A ₄₃₇	0.436
A ₄₃₈	0.437
A ₄₃₉	

times added by either the manufacturer or the fabricator. Molding temperatures, catalyzing and emulsifier changes, the same color shifts (density change), which in turn are affected by catalyst systems and temperature. Also, aging of color of the original resin for the purpose of uniformity. In the lighter or darker resin intended for applications where descriptive colorations or high light transmission are factors, color control of the resin becomes even more important.

The Gardner-Hellige viscosity comparative standards are generally employed as an in-process control for polymers. The final resin color properties being judged by A.P.E.A. standards. Table II-13 presents brief descriptive comparison of these two with other methods applicable in evaluating color of liquid polymer resins.

Index of Refraction. Refractive index is defined as the ratio of the speed of light in a vacuum to its speed in the substance considered. It has some relationship to polymers to the possibility of matching the index of refraction of the transparent or translucent materials. A perfectly transparent laminate has not yet been marketed commercially, however.

TABLE II-12. COMPARISON OF SYSTEMS FOR COLOR EVALUATION OF LIQUID POLYESTER RESINS

System	Range for Polymer	Resins in this with Polymer	Remarks
Gardner-Hellige	1-5 Light to dark amber	For control during esterification process	Use viscosity sample in bubble tubes. Evaluate by matching color values (ASTM-D1544).
A.P.E.A. (Glass)	0-200 (Light to dark)	Finished resin control (with or without fillers or additives)	Use long-form Nessler tubes. Evaluate against platinum-cobalt solution standards for color intensity (ASTM-D1556).
Spectral transmission	0-100% at specific wave length	For special property measurements or comparisons	Use spectrophotometer. Evaluate against standard color density which is not in all cases practical for control and processing specifications (A.O.C.S. method C-19-40).
Lovibond, etc.	Red-60.0 Yellow-100.0 Blue-0.20	Provides separation of gray and green tints in polymers by using the red and yellow tinted glasses. The gray and green tints are not resolved using the Gardner system.	Use color-reading apparatus described in A.O.C.S. official method C-19-44.

resin (N₂) gas is less soluble in polyester than carbon dioxide; therefore, there is more likelihood of entrained gas in the resin if carbon dioxide has been used in production as the inert-gas blanket.

Tests on Liquid-catalyzed Resins

Gel-Point Tests. Several tests, both principally around the "gel time" of a polyester resin, are employed to define its mechanical or physical behavior in the ultimate molding or forming operation, and, in addition, its storage stability, tank life, or gel-time drift.

Actually, the mechanism or physical changes by which polyester resins gel and cure is related to three separate phases, all related to and varying with the reactivity of the resin, the inhibitor, the catalyst used, and the curing temperature. Gelation is defined by the point at which the resin, after being catalyzed, ceases to be a viscous liquid and becomes a soft, elastic, rubbery solid. In layup or press molding, flow ceases after gelation, and no further changes may be made in any aspect of molding the product. Secondly, there is an intermediate stage in which the gel thickness or becomes slightly harder, and the temperature increases slightly, whatever the temperature range in which the molding is being carried out.

Thirdly, a strong exotherm occurs, brought on by the full result of the chemical action of polymerization. This accounts for the curing in some types of molding, and adds to it in other types. Although polyester moldings and laminates are "wet" and for the most part usable when reduced to room temperature following the exothermic reaction, ultimate properties are not always immediately developed, and in many cases a postcure is desirable.

Several different but related methods of defining gel time, or of using gel time to describe differences in various types of polyester, or to compare similar types have been known and are in general usage. Due to their similarity, an attempt has been made to tabulate these methods in Table II-13. A more detailed discussion of gelation and exotherm is included under "Catalysis" in this chapter.

While the gelation methods presented in Table II-13 represent the optimum or usual requirements for the processes briefly referred to, it should be realized that variation in conditions and amounts of catalyst can greatly vary the resultant gel time. Hence, gel-time

measurement is a manufacturing tool as well as a material control. Practical experience has shown the advantage of conducting gel-time tests at the temperatures employed in manufacturing or fabricating, as well as at 120° or 180°F, if the two temperatures are different.

Air Inhibition. The surface properties of a polyester resin immediately following gel and cure may be evaluated by first spreading a resin film on a glass plate using a film applicator (define thickness of film to 0.010 in. or 0.020 in.), allowing it to cure at room or elevated temperature as required, and testing the surface for tack or adhesion with thin glass paper or a probe. All polyesters are naturally inhibited by contact with the atmosphere during cure, due partially to styrene volatilization. Some compositions react less than others. For resins which must cure in contact with air (hand lay-up, spray-up), there is added, either in the thinning kettle or as-cured, an ingredient that migrates to the surface during cure and forms a thin film which actually prevents contact of the resin material with air.

Tests on Cured Solid Resins

Mechanical Properties. The mechanical and electrical properties of laminated, reinforced polyester (and other) resins are of prime importance in actually describing end-use performance, and are fully discussed in Section VIII. However, the properties of cast polyesters (unfilled and unweathered) are useful not only in comparing the type of resin (rigid, resilient, or flexible) but also in the control of properties. This is true because several properties of cast resins, although not as high in ultimate values as a fiber glass-reinforced laminate made from the resin in question, show greater deviation or fluctuation from specific values due to composition changes or cure variations. For this reason, cast resin properties can be used as a means of control, as well as fulfilling their specific function.

Table II-14 presents a comparison of mechanical properties of three representative polyester resins (rigid, resilient, and flexible) in the cast, unfilled, unweathered state, with a typical cloth laminate made using the rigid resin. The 12-PP, 181-45%₂, glass-treated cloth laminate will be considered a standard laminate for comparison purposes, and will be used elsewhere in this book.

The only test not referred to previously or not

TABLE II-14. TYPICAL MECHANICAL PROPERTIES OF REPRESENTATIVE UNFILLED, UNREINFORCED POLYESTER CASTINGS COMPARED TO PROPERTIES OF A REPRESENTATIVE FIBER GLASS-REINFORCED LAMINATE*

[illegible]

Other resin types similar to unsaturated polyesters are briefly described, with the main differences shown:

Allyl Reacts. These resins are composed of original reaction ingredients similar to those of the unsaturated polyester, but are modified with fatty acid oil types (linseed, soy, etc.) instead of monomers. No catalyst is added, but curing is accomplished by air-drying or baking in which oxygen provides the cross-linking resins; thus the reaction is still a type of addition polymerization. The principal application of allyls is in coatings and paint.

Some resins termed alkyds, but falling into the "unsaturated polyester" class, are monomeric and have had catalyst added. These are usually available as high-pressure molding compounds, ready-mixed with filler and reinforcement.

Saturated Polyesters. These are fusible resins in which none of the original ingredients are unsaturated, no monomer or catalyst is required, and the resultant linear (uncross-linked or non-three-dimensional) polyester is formed directly from the original melt into the product (fibers or film) and becomes a finished resin as it reaches room temperature.

Included in ASTM designations is an impression type hardness gauge test. (See footnote, Table II-1A.)

DESIGN CHEMISTRY

Rechts Ingepöndel

The resins commonly referred to as unsaturated polyolefins are mixtures of the true ester (long-chain polymer which results from the beta reaction) dissolved in a polyunsaturatable monomer which provides cross-linking units to the chains three-dimensionally. The two components react or copolymerize upon introduction of a peroxide (or equivalent type) catalyst to form a rigid, inflexible thermoset.

The terminology, "unsaturated," indicates easily to form a rigid, unreactive thermoset. The thermosetting, "unsaturated," indicates that unreacted double bonds are carried over from the original (feed) ingredients into the finished resin to provide points of reactivity; the double bonds (unsaturations) are opened up by the free-radical catalyst and unite with similar reactive chemical groups or units of the monomer. The final curing reaction is classed as "addition" polymerization because no by-product results, as opposed to phenololics (condensation polymerization).

TABLE II-13 METHODS FOR DETERMINING AIR TOXICS

[illegible]

DEVELOPING CULTURE PROMOTERS

2

Foam Polyesters. These do not need unsaturation, but require excess hydroxyl groups for cross-linking with a diisocyanate monomer (usually toluene diisocyanate). They also require different catalysts (amines). A liquid that is easily volatized by a slight increase above room temperature is usually added as a blowing agent. An equally effective but more costly method of inducing foaming is by inclusion of excess carbonyl groups, which function both by cross-linking and by evolving carbon dioxide during gelation. Water, turning to steam, has also been used as a blowing agent together with CO₂ from the diisocyanate. Polyester resins are preferred for flexible foams.

Unsaturated polyesters are of major interest as reinforcement plastics due to the wide variety of climates and properties which may be obtained by varying the many potentially usable raw materials. These raw materials fall into four classes:

(1) *Unsaturated polybasic acids* are so termed because of the doubly bonded pairs of carbon atoms included in the aliphatic molecular structure, which contains two or more carbonyl (COOH) radicals. These introduce high reactivity and rigidity into the cross-linked polyester by providing the unsaturated double bond. Anhydrides contain one less molecule of water than the straight acids, e.g., maleic acid.

(2) *Saturated aromatic polybasic acids*, when included as a polyester resin ingredient, modify to some extent the rigidity introduced by the unsaturated polybasic acids. As with styrene, the unsaturation contained within the benzene ring structure does not enter into polymerization. There is no unsaturation outside the ring, the carbonyl groups being held by a single bond. These materials behave like saturated acids, but do not provide complete flexibility because of their rigid ring structure which is unlike the loose aliphatic structure of the saturated acids, e.g., phthalic and isophthalic acids.

(3) *Saturated aliphatic acids*, in which carbonyl groups are in an aliphatic structure, but in which no unsaturation exists, are used to modify the resin reactivity by introducing longer chain lengths between the cross-linking functions, resulting generally in the more resilient or flexible, higher molecular weight resins, e.g., adipic acid.

(4) *Polyhydric diols* (polyols), so termed because two or more hydroxyl (OH) groups exist

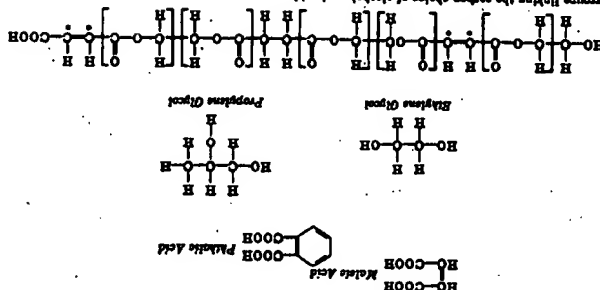
on each aliphatic glycol chain, react with either type of dibasic acid to form the ester groups. Many glycols are usable for polyester synthesis, and properties imparted are varied, ranging from rigidity to mellowness through water and heat sensitivity, e.g., ethylene glycol.

In formulating for the esterification reaction, one equivalent of acid requires one equivalent of glycol for complete esterification. A small excess (5 to 20%) of glycol is often used to bring the acid number down to a low value before polymerization has proceeded too far. The amount of water formed corresponds to the number of equivalents involved in the esterification. For each acid equivalent, one mole (18 grams) of water is formed. In the case of the acid anhydrides, only one-half mole of water is formed per acid anhydride equivalent (or, one mole per molecule of anhydride).

Hence, the organic reaction between acid and alcohol contrasts with the inorganic acid-base reaction in that the ester produced is vastly different from the secondary inorganic salt. The ester actually forms a polymer via a chemical growth process in which many single molecular units join to form a large, long-chain macromolecule, which is further added to and copolymerized by monomers and catalyst upon curing. The finished salt remains a simple, low molecular-weight entity.

The fundamental dibasic acid (5) plus ethylene alcohol (6) to form the polyester resin (7) may be represented by the chemical equation page 25. The esterification of polyester formation is greatly aided by development of the concept of "functionality." Functionality of polymeric molecules is expressed as the number of reactive points in a molecule that function in tying it to some other molecule. Ideally, if the functionalities of either of two or more reacting molecules is only 1, no polymer will be formed. If the functionality of both molecules is 2, a thermoplastic will result; if one reacting molecule has a functionality of 3 or more and the other has a functionality of 2 or more, a cross-linked thermoset polymer can result.

The inclusion of molecular weight in any discussion of polyesters is equivocal. Average molecular weight of the esterified polyester (before monomer addition and final cure) ranges in value from 800 to 5000. Varying the relationship of the acid and alcohol provides the greatest control over molecular weight. A general in-



RESEARCH, CATALYSTS, PROMOTERS

- Effect on the most important properties of the resulting resin. However, permitting the addition to grow too rapidly, or providing excessive chain branching (by use of polyhydric alcohols) provides a rapid build-up of molecular weight which is difficult to control,¹⁰ and may result in undesirable prepolymers during esterification.
- Average polymer molecular weight may be increased by the following methods:
 - Addition of inhibitors during esterification.
 - Reacting for longer time at lower temperature.
 - Addition of the unsaturated acid to the reaction only after the saturated acid and glycol have been reacted to an acid number of 80 or less.
 - Blending a low (20) acid-number resin

- Effect on the most important properties of the resulting resin. However, permitting the addition to grow too rapidly, or providing excessive chain branching (by use of polyhydric alcohols) provides a rapid build-up of molecular weight which is difficult to control,¹⁰ and may result in undesirable prepolymers during esterification.
- Average polymer molecular weight may be increased by the following methods:
 - Addition of inhibitors during esterification.
 - Reacting for longer time at lower temperature.
 - Addition of the unsaturated acid to the reaction only after the saturated acid and glycol have been reacted to an acid number of 80 or less.
 - Blending a low (20) acid-number resin

TABLE II-LA POLYESTER BAY MATERIAL INCORPORATION^a[illegible]

agreement between the different methods. Acid number determination continues to provide the most precise indication of molecular weight, and most polymer values of 10 to 15 being indicative of higher molecular weight in resins.

Table II-15 presents a survey of information available in the literature regarding the effect on cured polyester castings (from hand sand) when any particular acid or glycol is used.

AND THEIR EFFECT ON COASTAL BATH PROPERTIES

[illegible]

RESINS, CATALYSTS, PROMOTERS

22

Much of the data sources starting with a reagent type resin (1:1 maleic:phthalic anhydride + 2.0 diethylene glycol) with modified catalysts made. Growth in rigidity with increasing catalyst and toward flexibility by reducing the longer-chain anhydride. Addition of a "softener" prevents specific performance. Styrene monomer at 20% addition in the resin, however, and all results represent those on 1/4 in. thick castings cured with 1% DPO catalyst or equivalent.

Finally, qualification of the entire resin composition is necessary for complete representation of the performance of any particular ingredient. Some limitations prevent inclusion of the many details available in the literature. Table II-12 attempts to represent the best performance known for a given ingredient, "high" or "good" signifying the top or best value of three grades, thus this terminology is commonly used in the literature. Absence of any indicated performance of an ingredient for a specific property merely signifies that no reference was found in the literature cited.

Monomers

Table II-13 lists eight of the most commonly used or thoroughly investigated monomers, together with their physical properties and a qualitative summary of their influence on the physical properties of the cured polymers in which they might be used as cross-linkers. As in Table II-12 (listing polyester resin materials ingredients), many specific qualifications exist for monomers which are detailed in the literature.¹⁰

In Table II-17 is presented for further reference a list of additional materials used or potentially usable as monomers to create a specific function or property. Styrene was originally used, and due to its economics it has become the most generally employed monomeric material. Actually, almost any of the common compatible vinyl-unsaturated organic compounds which will either homopolymerize or copolymerize with other reactive materials may be used as a monomer. In many circumstances, improvement of cured laminate properties is brought about by establishing the crosslinking of a mixed monomer system.

During the pre-catalyzed stage, the base resin-monomer combination is only a simple liquid solution. After having been mixed in the thinning bath, very little conversion takes place,

and as much as 90% styrene or other monomer actually present can be recovered by carrying a vacuum distillation. During the pre-catalyzed stage, one of two or three per cent of monomer will combine with the base resin, detectable also as the amount removable by vacuum and by a rise in viscosity (molecular weight increase).

When the base resin-monomer mixture is catalyzed and cured in a mold, the unreacted resin or copolymer with the reactive groups of the active groups of the monomer readily combine with the resin after the latter have been attached and opened by the free radicals catalyzed. The resultant three-dimensional, cross-linked thermoset structure may be made to yield many and varied properties depending upon the type and amount of both base-resin ester and monomer.

Between one and two moles of styrene are required for each mole of unsaturated acid in the original ester.¹⁰ A combination as low as 1:1 probably leaves some unreacted double bonds. However, the optimum styrene (or other monomer) content will vary with the per cent of unsaturated acid present and with the molecular weight of the base-resin chain. Practically, monomer additions of from 5 to 50 per cent by weight are generally made by the resin manufacturer with minor adjustments made by the end user. The ultimate monomer content is dictated by the end-use viscosity requirements, and the desired finished laminate properties are determined empirically.

Inhibitors

Some type of chemical inhibition is necessary in any one of four phases of polyester manufacture or usage:

- Batch ingredients must be treated at the start of the esterification reaction to prevent random free radicals from inducing premature polymerization in the batch.
- Stability in storage is provided by adding the correct amount of the proper inhibitor. If the original inhibitor addition is depleted, more must be added in the thinning bath, as determined by gel-time tests.
- Extra inhibitors are sometimes desirable to nullify any tendency of the resin to gel prematurely due to heat or light in the intermediate or end-use process such as mixing, milling, or prolonged elevated temperature handling.
- All monomers necessarily contain inhibi-

TABLE II-13

Monomer	Chemical Structure	Boiling Point, °C	Freezing Point, °C	Density, g/cm ³	Refractive Index, n _D ²⁰	Specific Gravity
Styrene	<chem>C1=CC=CC=C1</chem>	146	-30	0.905	1.457	0.905
Acrylonitrile	<chem>C#CC=C</chem>	78	-78	0.789	1.360	0.789
Methyl Methacrylate	<chem>CC(=C)C(=O)OC</chem>	116	-78	0.930	1.411	0.930
Butyl Methacrylate	<chem>CCCCC(=C)C(=O)OC</chem>	163	-78	0.880	1.411	0.880
Hexyl Methacrylate	<chem>CCCCCC(=C)C(=O)OC</chem>	205	-78	0.830	1.411	0.830
Octyl Methacrylate	<chem>CCCCCCC(=C)C(=O)OC</chem>	247	-78	0.780	1.411	0.780
Dodecyl Methacrylate	<chem>CCCCCCCCC(=C)C(=O)OC</chem>	289	-78	0.730	1.411	0.730
Stearic Acid	<chem>CCCCCCCCCCCCCCCC(=O)O</chem>	339	69	0.940	1.470	0.940
Palmitic Acid	<chem>CCCCCCCCCCCC(=O)O</chem>	311	6	0.880	1.470	0.880
Myristic Acid	<chem>CCCCCCCC(=O)O</chem>	281	-16	0.820	1.470	0.820
Lauroic Acid	<chem>CCCCCCCC(=O)O</chem>	254	-9	0.760	1.470	0.760
Caproic Acid	<chem>CCCC(=O)O</chem>	205	-1	0.700	1.470	0.700
Valeric Acid	<chem>CCCC(=O)O</chem>	187	-4	0.640	1.470	0.640
Butyric Acid	<chem>CCCC(=O)O</chem>	163	-8	0.580	1.470	0.580
Propionic Acid	<chem>CCCC(=O)O</chem>	141	-18	0.520	1.470	0.520
Acetic Acid	<chem>CC(=O)O</chem>	118	-17	0.460	1.470	0.460
Formic Acid	<chem>CC(=O)O</chem>	100	-8	0.400	1.470	0.400

TABLE II-17. AROMATIC MONOMERS

Monomer	Function or Remarks
1. Methyl acrylate	Improved light stability; weakens mechanism of inhibition; improves strength of catalyst; similar to No. 10.
2. Ethyl acrylate	Similar to No. 10.
3. Allyl methacrylate	More reactive with catalyst; improves strength of catalyst; similar to No. 10.
4. Acrylonitrile	More reactive with catalyst; improves strength of catalyst; similar to No. 10.
5. Vinyl acetate	Similar to No. 10.
6. Vinyl phenol	Similar to No. 10.
7. Methyl methacrylate	Similar to No. 10.
8. Ethyl methacrylate	Similar to No. 10.
9. n-Butyl methacrylate	Similar to No. 10.
10. Methyl methacrylate	Similar to No. 10.
11. Allyl diphenyl ether	Similar to No. 10.
12. Diethyl phenyl ether	Similar to No. 10.
13. Methyl phenyl ether	Similar to No. 10.
14. Diethyl ether	Similar to No. 10.
15. Methyl ether	Similar to No. 10.
16. Triethyl ether	Similar to No. 10.
17. Triethyl ether	Similar to No. 10.
18. Triethyl ether	Similar to No. 10.
19. Triethyl ether	Similar to No. 10.
20. Triethyl ether	Similar to No. 10.
21. Triethyl ether	Similar to No. 10.
22. Triethyl ether	Similar to No. 10.
23. Triethyl ether	Similar to No. 10.
24. Triethyl ether	Similar to No. 10.

References: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100.

tion to prevent homopolymerization in storage. Some of the less reactive monomers do not require inhibition.

TABLE II-18. AROMATIC MONOMERS

Monomer	Function or Remarks
1. Methyl acrylate	Improved light stability; weakens mechanism of inhibition; improves strength of catalyst; similar to No. 10.
2. Ethyl acrylate	Similar to No. 10.
3. Allyl methacrylate	More reactive with catalyst; improves strength of catalyst; similar to No. 10.
4. Acrylonitrile	More reactive with catalyst; improves strength of catalyst; similar to No. 10.
5. Vinyl acetate	Similar to No. 10.
6. Vinyl phenol	Similar to No. 10.
7. Methyl methacrylate	Similar to No. 10.
8. Ethyl methacrylate	Similar to No. 10.
9. n-Butyl methacrylate	Similar to No. 10.
10. Methyl methacrylate	Similar to No. 10.
11. Allyl diphenyl ether	Similar to No. 10.
12. Diethyl phenyl ether	Similar to No. 10.
13. Methyl phenyl ether	Similar to No. 10.
14. Diethyl ether	Similar to No. 10.
15. Methyl ether	Similar to No. 10.
16. Triethyl ether	Similar to No. 10.
17. Triethyl ether	Similar to No. 10.
18. Triethyl ether	Similar to No. 10.
19. Triethyl ether	Similar to No. 10.
20. Triethyl ether	Similar to No. 10.
21. Triethyl ether	Similar to No. 10.
22. Triethyl ether	Similar to No. 10.
23. Triethyl ether	Similar to No. 10.
24. Triethyl ether	Similar to No. 10.

References: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100.

tion to prevent homopolymerization in storage. Some of the less reactive monomers do not require inhibition.

TABLE II-19. AROMATIC MONOMERS

Monomer	Function or Remarks
1. Methyl acrylate	Improved light stability; weakens mechanism of inhibition; improves strength of catalyst; similar to No. 10.
2. Ethyl acrylate	Similar to No. 10.
3. Allyl methacrylate	More reactive with catalyst; improves strength of catalyst; similar to No. 10.
4. Acrylonitrile	More reactive with catalyst; improves strength of catalyst; similar to No. 10.
5. Vinyl acetate	Similar to No. 10.
6. Vinyl phenol	Similar to No. 10.
7. Methyl methacrylate	Similar to No. 10.
8. Ethyl methacrylate	Similar to No. 10.
9. n-Butyl methacrylate	Similar to No. 10.
10. Methyl methacrylate	Similar to No. 10.
11. Allyl diphenyl ether	Similar to No. 10.
12. Diethyl phenyl ether	Similar to No. 10.
13. Methyl phenyl ether	Similar to No. 10.
14. Diethyl ether	Similar to No. 10.
15. Methyl ether	Similar to No. 10.
16. Triethyl ether	Similar to No. 10.
17. Triethyl ether	Similar to No. 10.
18. Triethyl ether	Similar to No. 10.
19. Triethyl ether	Similar to No. 10.
20. Triethyl ether	Similar to No. 10.
21. Triethyl ether	Similar to No. 10.
22. Triethyl ether	Similar to No. 10.
23. Triethyl ether	Similar to No. 10.
24. Triethyl ether	Similar to No. 10.

References: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100.

tion to prevent homopolymerization in storage. Some of the less reactive monomers do not require inhibition.

TABLE II-19. Representative Temperature & Curing Systems Based on Polyurethane Resins

Type of Cure	Typical Catalyst/Promoter System	Designation of Typical Polymer
1. Delayed or B Stage: Reinforcement saturated by resin with extended catalyzed stability (resin usually contains DAP monomer), cured at 23-30°C, 24-40 min.	1% benzoyl peroxide	Prepreg
2. Room temperature-cured cure (12-24 hr)	1% methyl ethyl ketone peroxide plus 0.05% cobalt naphthenate (or less)	Thick coatings
3. Room temperature-rapid cure (20 min-2 hr)	0.4 to 1.5% MEK peroxide plus 0.1 to 0.5% cobalt naphthenate or: 1% BPO plus 0.25 to 0.1% di-methyl saliline	Hand lay-up or spray-up
4. Autoclavable cure (less) Stage 1: 150-180°C-20 min. Stage 2: 200-230°C-30 min.	0.25% BPO plus 0.2-1.0% amine hydroperoxide plus 0.25% amine promoter	Architectural sheet
5. High-temperature cure (press) Time-20 to 60 min. Temperature-225 to 300°C. Pressure at higher temperatures when required.	0.5 to 1.5% BPO or 1% tert-butyl hydroperoxide or 1% tert-butyl peracetate	Machined die and performance and cast; laminates

What means are available for generally triggering addition polymerization? There are four: thermal or photochemical means, for which no chemical catalyst is required; and either free radical or ionic means, which involve catalysts. Free radicals are essentially responsible for polyester polymerization, and these are most generally applied from decomposition by heating, or action of a promoter on an organic peroxide. The peroxides are referred to as catalysts, but are not so in the truest sense, because they are consumed in the polymerization reaction. There is evidence that residual portions of free radicals exist in the network of the final product.

Assuming that a dihydric acid-dihydric alcohol monomer polyester is activated with an organic peroxide, the following mechanism is set in motion:

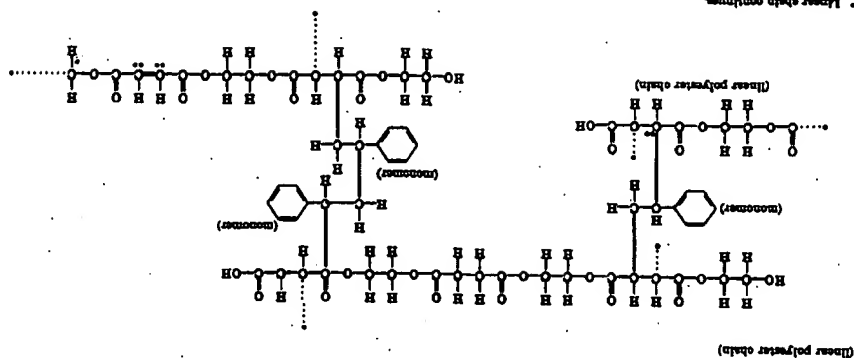
- The organic peroxide, represented as $R-O-O-R$, where R and R' may be an alkyl or aryl radical or hydrogen, decomposes by homolytic cleavage of the $O-O$ bond to release the $R-O$ and $R'-O$ free radicals.
- The free radicals first react with the chemical inhibitor which has been previously added to the resin, since the inhibitor material

must be chemically dissipated before any reaction between free radicals and the $C=O$ double bond can proceed. The number of free radicals available for polymerization can be directly influenced by accelerators (if present) and inhibitors, and the rate of peroxide decomposition (free radical production) must be such as to provide for the desired rate of consumption of the inhibitor, and the desired speed of polymerization.

- Apparently, the free radicals serve to open the double bond in the polyester linear chain to set in motion that portion of the polymerization process designated as initiation. Either the opened double bonds react with the vinyl groups of the monomer, or the free radicals serve to also open (add to) these latter unsaturated $C=C$ bonds, permitting them to perform their cross-linking function, uniting the polyester chains into a three-dimensional network. There is further evidence that free radicals may also, to some degree, react with the unsaturated monomer to form various products of decomposition. The following formula represents the chain-jointing and network growth schematically* (page 25):

d) The processes which are descriptive of

POLYESTER RESINS



continuation of polymerization are termed "propagation" (or chain growth) and "termination." The functionality of the resin, as well as the types and concentrations of inhibitor, promoter, and catalyst determines the rate at which propagation proceeds. Also, the extent of chain growth is limited by the number of reactive sites available for cross-linking thereby creating rigid or even double bonds. Termination of polymer growth occurs via reactions designated as depropagation, disproportionation, coupling and chain transfer. Also, high viscosity or "gel" formation during polymerization will cause termination.

Theoretically, the reaction of polyesters should go to completion with all double bonds reacted upon by free radicals and complete cross-linking established under the most favorable conditions. However, in actual practice, as determined by laboratory methods, the true amount of residual unsaturation (indicating low extent of polymerization) has not been traced in the actual curing of polyesters, and may be summarized as follows:

- As stated previously, less than 1% of the unsaturated double bonds are reacted in the pre-catalyzed base polyester-consumer combination.
- After catalyzing and polymer "initiation," when chain propagation has progressed so that 25 to 40% of the unsaturation has been taken up, gelation occurs. The gel hardness and initial volume shrinkage of the resin occurs as propagation proceeds, and 40 to 60% of the total conversion is converted.
- An incomplete cure exists when a total of 80% of the unsaturation has been utilized without the development of full properties.
- What may be considered as an optimum cure with full properties potential realized occurs when 92 to 96% of the unsaturation has been converted. Neither extra catalyst nor post-curing will convert this slight amount of remaining unreacted material, which is sometimes removable from the cured resin by solvent extraction, but may be more accurately determined by analytical methods.

The failure of all unsaturated sites to become reacted during final cure accounts for the discoloration of polyesters upon weathering and long-term aging. The unreacted double bonds eventually take up oxygen due to the action of

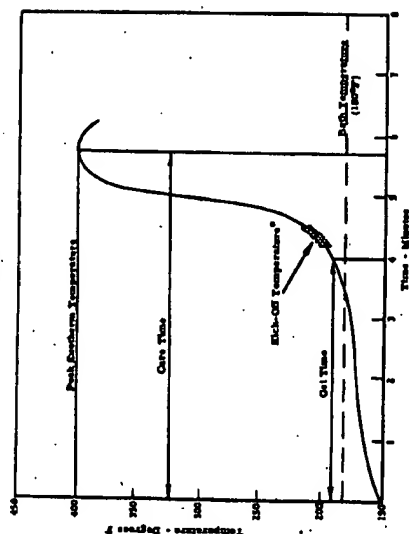


Figure 11-14. 1977 standard EPI endotherm curve for polyester resin containing 1% base catalyst. Note: Black-off temperature is not included as part of the standard EPI gel-time test.

specific resin of changes in concentration of catalyst, promoter, and filler. Table II-11 illustrates the changes induced by catalyst content and base-temperature variations in the standard endotherm constants of a general-purpose self-cure type polyester (1.0 mils thick, 1.0 phthalic acid No. 45-50; 7 parts allyl to 3 parts styrene, viscosity = 12 poise).

Fillers (and reinforcements), being inert, lower the peak endotherm temperature of a resin formulation by absorbing heat from the reacting resin, but lengthen the gel time only if a room temperature cure is used, or if inhibitory effect is contributed.

Promoters are discussed later, since their function is to augment and expand the ranges of action of the catalyst. They are also the major factor governing the rate of the appropriate organic peroxide for use in initiating polymerization in polyester resins. However, ease of handling and mixing, processing temperature and time, and rate of reaction are also pertinent.

The many interesting properties found in the various peroxides are listed in Table II-12. All

Table II-10. Variations in Organic Catalysts or Base, Promoters and Fillers. 1977 EPI Standard Endotherm Constants. 1977 EPI Standard Endotherm Constants. 1977 EPI Standard Endotherm Constants. 1977 EPI Standard Endotherm Constants.

	1977 EPI	1977 EPI	1977 EPI	1977 EPI
Old time, min-sec	4-25	4-30	4-35	4-40
Cure time, min-sec	9-25	9-30	9-35	9-40
Peak endotherm °F	325	330	335	340

Base Catalyst Allied Chemical Corp.

TABLE II-11. EFFECT OF VARIATIONS IN CATALYST CONCENTRATION AND BATH TEMPERATURE ON THE DECOMPOSITION OF A GENERAL-PURPOSE POLYMERIZATION

Temp, °C	Conc, %	k_d , hr ⁻¹	k_d , hr ⁻¹	k_d , hr ⁻¹
10.5	10.3	13.4	300	305
1.0	4.0	7.3	325	192
2.0	2.0	3.3	435	180
4.0	1.0	1.3	415	135
6.0	0.5	0.3	430	135
Temp, °C	Conc, %	k_d , hr ⁻¹	k_d , hr ⁻¹	k_d , hr ⁻¹
150	4.4	0.3	430	300
210	1.0	2.7	430	300
240	1.3	2.1	430	300

though only approximately one-half the peroxide listed are in routine commercial use as polymer curing agents, all have been evaluated for potential or comparative performance in polymerization on the basis of considerations given in the following discussion of the vertical column headings:

a) *Free-radical activity*: The available free-radical activity, and concentration plus typical chemical structure, are indicated.

b) *Half-life data*: In order to establish a basis of comparison, the chemical kinetics were studied (Machett and Maggs) for decomposition of one-half the amount of a low (0.1 or 0.3 g-moles of peroxide group per liter) concentration of each peroxide in benzene through a temperature range (150–250°C) corresponding to end-use polymer processing. The thermal decomposition of peroxide in solvent is not a free-radical reaction. It is actually meaningless to refer to the time necessary for 100% of a material such as an organic peroxide to decompose, because theoretically, an infinite time is required. Therefore, half-life becomes a convenient parameter of peroxide activity.

Based on the residual peroxide concentration after specific test intervals at various temperatures, and applying first-order reaction rate calculations, the half-life ($t_{1/2}$) was in turn calculated from

$$k_d = \frac{0.693}{t_{1/2}}$$

where k_d is the first-order rate constant. Following the log k_d was plotted against $1/T$ (T = absolute temperature) and showed essentially straight-line relationships for almost all the peroxides tested. Reference times of one minute, 10 hours, and 100 hours were then selected, after which the temperatures required for decomposition of one-half of the peroxide at these intervals were selected from the curves and tabulated. These half-life data are reproduced in Table II-11.

Each peroxide can thus be evaluated for the order of peroxide or free-radical activity in terms of a large number of other peroxides. Also, since the original data curves can be extrapolated, it is possible to estimate the half-life of a peroxide at temperatures where it was impractical to make experimental determinations. As an example, half-lives for benzoyl peroxide were determined between 165 and 215°C, but the curve was further extended to provide data from which the following complete range of temperatures versus times for half-life decomposition was determined: 150°–100 hours; 165°–10 hours; 197°–1 hour; 237°–0.1 hour; 277°–1 min. From the data it is also noted that 2,4-dichlorobenzoyl peroxide (No. 3) is the most reactive peroxide, and would be expected to initiate reactions at the lowest temperature, while 3,3-dimethyl-1-benzyl-2,4-dichloroperoxide (No. 14) would require the highest operating temperatures to perform effectively.

c) *Activation energies (ΔE)* were calculated in the same way for all these peroxides which showed first-order decomposition. The activation energy may be determined from measurements of the specific rate constant (k_d) at two or more temperatures according to the following equation of plotting $\log k_d$ against the reciprocal of the absolute temperatures ($1/T$), the slope of the resulting straight line being equal to $\Delta E/2.303R$:

$$\log \frac{k_d}{k_d'} = \frac{\Delta E}{2.303 R} \left(\frac{1}{T} - \frac{1}{T'} \right)$$

where R = the universal gas constant (1.987 cal deg⁻¹ mole⁻¹).

Since for first-order decomposition (formula 9 for k_d applies), ΔE can be calculated from the slope of the line obtained by plotting $\log k_d$ versus $1/T$. The degree of slope of these lines is

a direct qualitative measure of the activation energy associated with each peroxide.

From a practical standpoint, peroxides with high activation energies will decompose over a narrower temperature range or provide a larger number of free radicals in a given temperature range, than those with low activation energies. Hence, if an initiator is required that will show a narrow decomposition range, a high activation energy is desired. If a slow, steady decomposition is required, a low activation energy would fill the need.

Although both relative peroxide activity and activation energy can be reliably changed by the introduction of a radical scavenger, the formation in the half-life and activation energy curves may be considered as basic data necessary for the choice of an effective initiator for any free-radical polymerization system.

d) *Half-life of peroxide*: In Table II-11, it was noted that the half-life of peroxide was depressed with increased catalyst concentration, and that gel and cure times correspondingly shortened. Also, as specified, the half-life of peroxide remained constant during changes in bath temperature used as a reference point for the temperature data in Table II-11. It is significant in that, by operating at or above the half-life of peroxide range for a particular initiator system, rapid cure can be obtained.

e) *Old Time Data*: Standard SFT gel time determinations for 1% of the commercial form of each peroxide listed were made in a 100°C bath (unless otherwise noted) using the reference polyester (formulas on page 37). These data are indicated for purposes of coordinating gel times with half-life data and half-life of peroxide to further study peroxide activity.

Determination of a reliable mathematical relationship between the rate of formation of active free radicals in a given peroxide and the gelation time of a normal unsaturated polyester would be difficult because of the many variables involved. However, a ten-hour half-life for many of the peroxides studied corresponded very nearly to the temperature at which a 15-minute gel time was obtained.

f) *Effect of Mixed Catalyst Systems*: Exothermic curves were run at 150, 115, 100°C. Total peroxide concentrations comprising an active oxygen content equivalent to that obtained with 1% benzoyl peroxide were investigated to determine subject data. Dystrophic, intermediate-to-

natural, and inhibitory effects were noted. The synergistic or catalytic effect of the peroxide combination and the time which showed inhibition are listed at the bottom of the tabulation, with reference made by number.

g) *Free-radical activity*: These organic peroxides employed as catalysts in commercial polymerizations are so indicated, and the temperature range in which they have been found to be most useful is also indicated. The functions of the organic peroxide when used as a catalyst for polymerization systems other than those for peroxide are briefly referred to.

In addition to those peroxides cited in Table II-11, it has recently been brought to light that certain types of epoxy-resin hardeners (epoxy resin) are used in place of glass-thermoforming resins as used with polyester polymerization initiators when used with or without peroxide catalyst. The epoxides themselves do not initiate free-radical polymerization, but undergo a free-radical reaction at the epoxy group.

Peroxides

Figure II-12 has been prepared to provide an illustration of the effect of two members of a specific group of chemical, termed "peroxides," in accelerating decomposition of peroxide esters. Interfering with polymerization at temperatures below the normal decomposition and activation temperatures of the particular peroxide.

For methyl ethyl peroxide, a half-life of 15 minutes at 200°C is achieved, and gelation occurs in approximately 15 hours in a standard polyester resin at room temperature for a concentration of 1%. Curve A compares how the temperature gel time may be shortened to 80 minutes by the incorporation of 0.4% of the peroxide, which implements (6% each resin), and further decreased to 10 minutes by additionally increasing 0.1 per cent directly oxides (Curve B), termed the "accelerated" catalyst. Note the particular effect of the ester cure (by DDA) in raising the peak exothermic temperature.

It is fairly well-known that a simple exothermic system such as cobalt naphthenate, used together with methyl ethyl peroxide peroxide, will develop optimum properties at a slow rate after gelation and cure. In the early days of hand lay-up usage, eight hours' total mold time was required to produce a large item such

POSTER BOARD

Material	Weight	Length	Width	Thickness	Notes
1. Heavy paper	1.00	11.00	17.00	0.01	1.00
2. Heavy paper	1.00	11.00	17.00	0.01	1.00
3. Heavy paper	1.00	11.00	17.00	0.01	1.00
4. Heavy paper	1.00	11.00	17.00	0.01	1.00
5. Heavy paper	1.00	11.00	17.00	0.01	1.00
6. Heavy paper	1.00	11.00	17.00	0.01	1.00
7. Heavy paper	1.00	11.00	17.00	0.01	1.00
8. Heavy paper	1.00	11.00	17.00	0.01	1.00
9. Heavy paper	1.00	11.00	17.00	0.01	1.00
10. Heavy paper	1.00	11.00	17.00	0.01	1.00
11. Heavy paper	1.00	11.00	17.00	0.01	1.00
12. Heavy paper	1.00	11.00	17.00	0.01	1.00
13. Heavy paper	1.00	11.00	17.00	0.01	1.00
14. Heavy paper	1.00	11.00	17.00	0.01	1.00
15. Heavy paper	1.00	11.00	17.00	0.01	1.00
16. Heavy paper	1.00	11.00	17.00	0.01	1.00
17. Heavy paper	1.00	11.00	17.00	0.01	1.00
18. Heavy paper	1.00	11.00	17.00	0.01	1.00
19. Heavy paper	1.00	11.00	17.00	0.01	1.00
20. Heavy paper	1.00	11.00	17.00	0.01	1.00

RESIN, CATALYST, PROMOTERS

Material	Weight	Length	Width	Thickness	Notes
1. Heavy paper	1.00	11.00	17.00	0.01	1.00
2. Heavy paper	1.00	11.00	17.00	0.01	1.00
3. Heavy paper	1.00	11.00	17.00	0.01	1.00
4. Heavy paper	1.00	11.00	17.00	0.01	1.00
5. Heavy paper	1.00	11.00	17.00	0.01	1.00
6. Heavy paper	1.00	11.00	17.00	0.01	1.00
7. Heavy paper	1.00	11.00	17.00	0.01	1.00
8. Heavy paper	1.00	11.00	17.00	0.01	1.00
9. Heavy paper	1.00	11.00	17.00	0.01	1.00
10. Heavy paper	1.00	11.00	17.00	0.01	1.00
11. Heavy paper	1.00	11.00	17.00	0.01	1.00
12. Heavy paper	1.00	11.00	17.00	0.01	1.00
13. Heavy paper	1.00	11.00	17.00	0.01	1.00
14. Heavy paper	1.00	11.00	17.00	0.01	1.00
15. Heavy paper	1.00	11.00	17.00	0.01	1.00
16. Heavy paper	1.00	11.00	17.00	0.01	1.00
17. Heavy paper	1.00	11.00	17.00	0.01	1.00
18. Heavy paper	1.00	11.00	17.00	0.01	1.00
19. Heavy paper	1.00	11.00	17.00	0.01	1.00
20. Heavy paper	1.00	11.00	17.00	0.01	1.00

TABLE II-12. PROPERTIES OF QUARTZ PROMOTERS

5

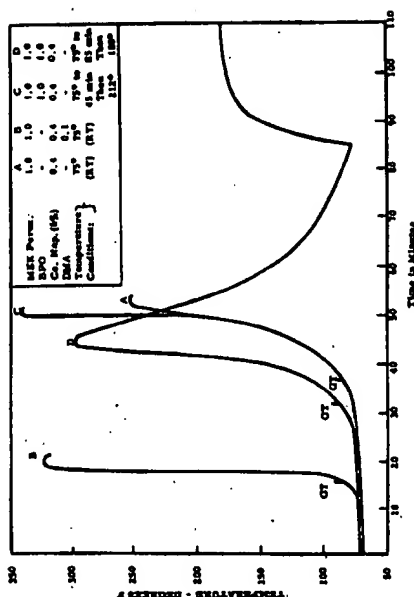


Figure 11.1.5. Endotherm curves for room-temperature curing systems in polyester resins.

as a heat by using a double-promoted system. The overall mold time was reduced to 24 hours without sacrificing mechanical properties developed in a 48-hour mold.

Curves *C* and *D* in Figure 11-24, plotted against time, show the additional heat developed in the two epoxy systems. In Curve *C*, the 15% EPO remained in the resin in samples placed in the MEEK solution and the sample placed in the 100% EPO bath at times of gelation. In Curve *D*, the 15% EPO and 1% MEEK premix in a standard polyether resin were gelled at room temperature under the influence of 0.4% cobalt naphthenate, and the sample was allowed to cure and pass through the cure cycle while maintaining ambient room-temperature conditions. Additional heat developed in a 100% EPO bath after the sample cooled to room temperature (35 minutes) did not initiate any further exothermic reactions in the resin due to the extra addition of the EPO. Conclusion: The extra additional catalyst or presence of a catalyst generally more reactive at elevated temperatures further advances a room-temperature cure by increasing the intensity of the exothermic reaction. However, once the resin has reached gelation,

As previously indicated, promoters are also used for specific applications as intermediates and

Temperature	Relative Humidity	Wind	Direction	Speed	Time	Remarks
7.0	65	10	SE	10	10:00	Light rain, clouds clearing.
7.0	65	10	SE	10	11:00	Light rain, clouds clearing.
7.0	65	10	SE	10	12:00	Light rain, clouds clearing.
7.0	65	10	SE	10	13:00	Light rain, clouds clearing.
7.0	65	10	SE	10	14:00	Light rain, clouds clearing.
7.0	65	10	SE	10	15:00	Light rain, clouds clearing.
7.0	65	10	SE	10	16:00	Light rain, clouds clearing.
7.0	65	10	SE	10	17:00	Light rain, clouds clearing.
7.0	65	10	SE	10	18:00	Light rain, clouds clearing.
7.0	65	10	SE	10	19:00	Light rain, clouds clearing.
7.0	65	10	SE	10	20:00	Light rain, clouds clearing.
7.0	65	10	SE	10	21:00	Light rain, clouds clearing.
7.0	65	10	SE	10	22:00	Light rain, clouds clearing.
7.0	65	10	SE	10	23:00	Light rain, clouds clearing.
7.0	65	10	SE	10	24:00	Light rain, clouds clearing.

SECRET-СТІ-П СТВУХ

TABLE II-1.13. COMPARATIVE EFFECTS OF COMMONLY USED PROMOTERS ON THE GEL AND CURS CHARACTERISTICS OF VARIOUS PEROXIDE CATALYSTS

Name of Compound		Conc. of solution (g./100 cc.)	10.0	12.5	15.0	17.5	20.0	22.5	25.0	27.5	30.0	32.5	35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5	55.0	57.5	60.0	62.5	65.0	67.5	70.0	72.5	75.0	77.5	80.0	82.5	85.0	87.5	90.0	92.5	95.0	97.5	100.0	102.5	105.0	107.5	110.0	112.5	115.0	117.5	120.0	122.5	125.0	127.5	130.0	132.5	135.0	137.5	140.0	142.5	145.0	147.5	150.0	152.5	155.0	157.5	160.0	162.5	165.0	167.5	170.0	172.5	175.0	177.5	180.0	182.5	185.0	187.5	190.0	192.5	195.0	197.5	200.0	202.5	205.0	207.5	210.0	212.5	215.0	217.5	220.0	222.5	225.0	227.5	230.0	232.5	235.0	237.5	240.0	242.5	245.0	247.5	250.0	252.5	255.0	257.5	260.0	262.5	265.0	267.5	270.0	272.5	275.0	277.5	280.0	282.5	285.0	287.5	290.0	292.5	295.0	297.5	300.0	302.5	305.0	307.5	310.0	312.5	315.0	317.5	320.0	322.5	325.0	327.5	330.0	332.5	335.0	337.5	340.0	342.5	345.0	347.5	350.0	352.5	355.0	357.5	360.0	362.5	365.0	367.5	370.0	372.5	375.0	377.5	380.0	382.5	385.0	387.5	390.0	392.5	395.0	397.5	400.0	402.5	405.0	407.5	410.0	412.5	415.0	417.5	420.0	422.5	425.0	427.5	430.0	432.5	435.0	437.5	440.0	442.5	445.0	447.5	450.0	452.5	455.0	457.5	460.0	462.5	465.0	467.5	470.0	472.5	475.0	477.5	480.0	482.5	485.0	487.5	490.0	492.5	495.0	497.5	500.0	502.5	505.0	507.5	510.0	512.5	515.0	517.5	520.0	522.5	525.0	527.5	530.0	532.5	535.0	537.5	540.0	542.5	545.0	547.5	550.0	552.5	555.0	557.5	560.0	562.5	565.0	567.5	570.0	572.5	575.0	577.5	580.0	582.5	585.0	587.5	590.0	592.5	595.0	597.5	600.0	602.5	605.0	607.5	610.0	612.5	615.0	617.5	620.0	622.5	625.0	627.5	630.0	632.5	635.0	637.5	640.0	642.5	645.0	647.5	650.0	652.5	655.0	657.5	660.0	662.5	665.0	667.5	670.0	672.5	675.0	677.5	680.0	682.5	685.0	687.5	690.0	692.5	695.0	697.5	700.0	702.5	705.0	707.5	710.0	712.5	715.0	717.5	720.0	722.5	725.0	727.5	730.0	732.5	735.0	737.5	740.0	742.5	745.0	747.5	750.0	752.5	755.0	757.5	760.0	762.5	765.0	767.5	770.0	772.5	775.0	777.5	780.0	782.5	785.0	787.5	790.0	792.5	795.0	797.5	800.0	802.5	805.0	807.5	810.0	812.5	815.0	817.5	820.0	822.5	825.0	827.5	830.0	832.5	835.0	837.5	840.0	842.5	845.0	847.5	850.0	852.5	855.0	857.5	860.0	862.5	865.0	867.5	870.0	872.5	875.0	877.5	880.0	882.5	885.0	887.5	890.0	892.5	895.0	897.5	900.0	902.5	905.0	907.5	910.0	912.5	915.0	917.5	920.0	922.5	925.0	927.5	930.0	932.5	935.0	937.5	940.0	942.5	945.0	947.5	950.0	952.5	955.0	957.5	960.0	962.5	965.0	967.5	970.0	972.5	975.0	977.5	980.0	982.5	985.0	987.5	990.0	992.5	995.0	997.5	1000.0																																																																																																		
Name of Compound	per-centage	Conc. of solution (g./100 cc.)	10.0		12.5		15.0		17.5		20.0		22.5		25.0		27.5		30.0		32.5		35.0		37.5		40.0		42.5		45.0		47.5		50.0		52.5		55.0		57.5		60.0		62.5		65.0		67.5		70.0		72.5		75.0		77.5		80.0		82.5		85.0		87.5		90.0		92.5		95.0		97.5		100.0																																																																																																																																																																																																																																																																																																																																																																																																																																						
			10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0	12.5	10.0

POSITIVE CATALYTIC PROMOTERS

the explicit instructions of the manufacturers to generate catalysts and use of each resin should be rigidly observed. The variation in gel time with temperature and catalyst concentration for a typical rapid room-temperature curing resin is shown in Table II-115. Similar data may be developed for intermediate-temperature (150°F) cures.

On-the-job use of promoters is also common practice, although more freedom is possible in the controlling of the amount to be added, provided the system must be taken to guard against quality variations in the crude oil or kerosene due to improper or insufficient mixing of the promoter. Several unique systems have been devised¹ to which a constant amount of solvent or compatible monomer containing the promoter (or catalyst) is added to each resin batch. The gel time may be maintained constant by varying sleep-temperature conditions by systematically or automatically varying the amount of promoter (or catalyst) contained in the solvent or monomer.

Apart from toxicity precautions, if and when called for, the artificial rules governing the handling of promoters in: do not mix them readily with any catalyst materials outside the reactor batch. Almost all promoters act as poisons for reducing agents and inhibit explosive reactions when placed in direct contact with peroxide catalytic materials.

APPLICATIONS

There are five major classifications of methods of processing Reinforced Plastics, simply listed as follows with subdivisions, and more fully described in Section IV, Molding Methods.

A. Manned Molding Methods: Involving hand lay-up, hot molding, extrusion, processing and injection molding. These methods employ lay-up use of preformed material, contact casting, sand-chamber casting, potting and encapsulation, potting, gel coats and other coatings, and moldable binder resins. Medium- to slow-speed room-temperature curing systems apply with the exception of the urethane and epoxide resins.

Formers are usually incorporated into the resin by the manufacturer to provide a balanced system with guaranteed mechanical and esthetic properties. A solution may be desirable for long-term stability. A solution may be desirable for long-term stability. A solution may be desirable for long-term stability.

ment, or applica-
tion submitted on p. 2.

Table II-14. Function of Various Promoters Used with Polyethylene Resins

Promoter	Possible action function
Inorganic Compounds:	
1. Butyl chloride	Effective initiator for polyethylene but are limited in application (see No. 1).
2. Hydrogen sulfide	These and other multivalent metals in a low oxidation state behave as promoters. Other ferrous and stannous salts are also applicable.
3. Stannous chloride	Acts as inhibitor with organic peroxide alone, but acts as accelerator with peroxide plus conventional promoter.
4. Ferrous chloride	Induces room-temperature cure rates of 1 to 10% with some conventional promoters. Stimulates curing of peroxide and organic oxides and hydroxides of barium, strontium, magnesium, and also calcium oxide.
5. Calcium hydride	H ₂ O, H ₂ O ₂ are effective as room-temperature promoters, but have no primary in high-temperature cure.
6. Calcium reducing agents	Widely used (0.1-1.0%) as room-temperature cure promoter with methyl ethyl ketone peroxide or cyclohexanone peroxide. Room-temperature systems using cobalt naphthenate as the sole promoter do not rapidly develop optimum properties as indicated by tensile and wet-strength reaction tests. An accessory promoter is desirable. Cobalt itself is also supplied in another more common form (Cobalt RE-24, containing a gel-forming catalyst) which is used in conjunction with methyl ethyl ketone peroxide. Cobalt naphthenate is gradually incorporated into the polymer matrix by the manufacturer. Both forms strongly color the resin and impart some tinging to the cured part; which can usually be masked with fillers or pigments. The cobalt itself present provides the true reaction with catalyst to release free radicals. An aromatic resin widely used (0.05 to 0.5%) as an accessory room-temperature cure promoter with cobalt naphthenate, and also as a room-temperature cure initiator with BPO catalyst. DMA is cheap and effective for fast gel and cure, but is toxic, malodorous, and is generally not desirable in gel ends and resin conversions to be exposed to sunlight and weather due to discoloration upon aging.
7. Organic Compounds:	
8. Cobalt naphthenate, 0%	Commonly provides a longer processing content than DMA for an equivalent gel time, but provides a shorter cure time, hence produces a lower molecular-weight polymer which is not quite as strong. DEA has some advantages over DMA in producing less gel time drift on aging after the promoter is incorporated into the resin. DEA is also cheap but is toxic and will produce discoloration upon aging.
9. Dimethyl sulfone	Similar to performance to DMA and DEA and generally used in similar applications. This promoter discolors more slowly and to a slightly lower degree, and is less toxic than DMA or DEA. However, it is more expensive and slightly slower or more sluggish in curing.
10. N,N'-dimethyl sulfone	Used together with 1,4-dibutyl naphthalene in promoting room-temperature gelation and curing using common hydroperoxide as catalyst.
11. N,N'-dimethyl-p-toluidine	Not commonly used.
12. N-phenylthioaniline	Not commonly used.
13. 1,4-dibutylthiuron	Not commonly used.

Table II-14. Continued

Promoter	Possible action function
14. N or 1,4-dibutyl naphthalene	Macropromoter provides a solution promoter exhibiting no discoloration on aging, and reportedly prevents air-inhibition on curing when used with aqueous naphthenate and 1,4-bis(hydroperoxide). However, they actually reduce gelation but do not cure by themselves, hence must be added only at the same time as the catalyst. Since the macropromoter gel the resin, and the catalyst cure, the two are acting independently or together. A cure rate of about 1% is obtained with 1,4-dibutyl naphthalene for only about 1% complete. Macropromoter also gives erratic gel time results when used as promoter in concentrations of less than 0.05%. They are malodorous and generally regarded as not being as effective for promoting as are the aromatic amines. Not commonly used.
15. Triphenylene diphosphite	Similar to 1,4-dibutyl naphthalene and others are inhibitors at room temperature in polyester resins, but show some activation effect when stored at elevated temperatures (117°F.). It is D-4-bis(hydroperoxide) conditions good room-temperature inhibition with minimum propagation of cure at elevated temperatures. Hydroperoxide derivatives are not in general use as promoters. Not commonly used.
16. Phosphorotriethyl chloride	Chelates resin at room temperature is difficult as for cobalt naphthenate. Not commonly used.
17. Hydroquinone derivatives	Discolors more strongly than cobalt naphthenate. No advantage over cobalt naphthenate.
18. Ferric acetyl acetate	No advantage over cobalt naphthenate. Discolors strongly.
19. Magnesium naphthenate or stannous	Shortens room temperature gel times of all peroxides except BPO and 1,4-bis(hydroperoxide). Basis of other proprietary promoters.
20. Stannous acetate	Used at 5% in resin promoted with 1,4-bis(hydroperoxide) for faster cure at higher temperatures. Not commonly used.
21. Ferric octoate	Same as above. Not commonly used.
22. Phenyl phosphine acid	Used 0.05 to 0.1%. More commonly used as a catalyst for the catalytic reaction of allyls.
23. N-butyl sulfite	Not commonly used.
24. Diphenyl hydroxyphosphine	Similar to dimethyl sulfone. Not commonly used.
25. p-toluenesulfonic acid	Similar to dimethyl sulfone. Not commonly used.
26. 4-tert-butyl dimethyl phosphine	Similar to dimethyl sulfone. Not commonly used.
27. 4-tert-butyl dimethyl phosphine	Similar to dimethyl sulfone. Not commonly used.
28. N-phenylthioaniline	Similar to dimethyl sulfone. Not commonly used.
29. N-phenylthioaniline	Similar to dimethyl sulfone. Not commonly used.
30. N-phenylthioaniline	Similar to dimethyl sulfone. Not commonly used.
31. Dimethyl phosphine	Employed (0.15 to 0.5%) for fast room-temperature cure of easily inhibited polyesters. Not commonly used.
32. Triethanolamine	Similar to performance to, but not as effective as DMA and DEA. Not commonly used.
33. Tri-n-propylamine	Similar to performance to, but not as effective as DMA and DEA. Not commonly used.
34. Tri-n-butylamine	Similar to performance to, but not as effective as DMA and DEA. Not commonly used.
35. Tri-n-pentylamine	Similar to performance to, but not as effective as DMA and DEA. Not commonly used.
36. Tri-n-hexylamine	Similar to performance to, but not as effective as DMA and DEA. Not commonly used.
37. Tri-n-octylamine	Similar to performance to, but not as effective as DMA and DEA. Not commonly used.
38. Sodium sulfonate or diethyl sulfonate	Used (0.01 to 1%) together with peroxide catalyst to obtain clarity in laminates. Not commonly used.
39. Methyl iodide	Methyl iodide (0.5-1.0%) stabilizes against discoloration caused by some peroxide catalysts, but laminates hardness is somewhat diminished. Not commonly used.

Table II-11A—Continued

Promoter	Resins under Resins
40. Quaternary ammonium compounds	Most quaternary ammonium chlorides are effective promoters, but some perform as inhibitors. The promoters may be effectively incorporated into the resin with stability, but produce discoloration. Several proprietary promoters are based on these compounds.
41. Hydrogen halides	Proprietary—difficult to promoting effect to quaternary ammonium chlorides.
42. Cobalt Isonitrate	Room-temperature cure promoter with cyclohexanone peroxide or methyl ethyl ketone peroxide. The cobalt metal ions are the active promoters, hence no advantage over cobalt naphthenate. Not commonly used.
43. Propylene diamine	Similar to cobalt naphthenate. Not commonly used.
44. Triethylamine	Similar to cobalt naphthenate. Not commonly used.
45. Methylene chloride	Similar to cobalt naphthenate. Not commonly used.
46. Ultraviolet radiation ^a	Free radicals are produced in polymers by action of artificial ultraviolet radiation (2000 Å), also by exposure to sunlight. Both will promote cure in polymers emulsified with benzil (5%) or benzoin (5%). Benzil is more stable and provides long pot life; benzoin is more reactive and is preferred. Both provide gel times of thirty minutes after exposure starts, even at 25°C. No peroxide catalyst is required, but may be used (BPO preferred). The total amount of initiator may be added into the resin with emulsifier. Benzoin is more stable than benzil, providing consistent results. Benzoin is more stable than benzil, providing consistent results. Benzoin is more stable than benzil, providing consistent results.

Free radicals are produced in polymers by action of artificial ultraviolet radiation (2000 Å), also by exposure to sunlight. Both will promote cure in polymers emulsified with benzil (5%) or benzoin (5%). Benzil is more stable and provides long pot life; benzoin is more reactive and is preferred. Both provide gel times of thirty minutes after exposure starts, even at 25°C. No peroxide catalyst is required, but may be used (BPO preferred). The total amount of initiator may be added into the resin with emulsifier. Benzoin is more stable than benzil, providing consistent results. Benzoin is more stable than benzil, providing consistent results. Benzoin is more stable than benzil, providing consistent results.

67. Ambient humidity^a

Free radicals are produced in polymers by action of artificial ultraviolet radiation (2000 Å), also by exposure to sunlight. Both will promote cure in polymers emulsified with benzil (5%) or benzoin (5%). Benzil is more stable and provides long pot life; benzoin is more reactive and is preferred. Both provide gel times of thirty minutes after exposure starts, even at 25°C. No peroxide catalyst is required, but may be used (BPO preferred). The total amount of initiator may be added into the resin with emulsifier. Benzoin is more stable than benzil, providing consistent results. Benzoin is more stable than benzil, providing consistent results. Benzoin is more stable than benzil, providing consistent results.

Temp, °F	0.5%	0.75%	1.0%
60	20	25	30
70	40	50	60
80	55	65	75

Note: Curing After Chemical Cure.

tion of prepolymer materials to a rotating form. High-temperature oven cures are employed. D. Extrusion methods, including solid rod stock, hollow tubing and piping, structural cross-

resistance to cracking, rigidity or resistance (affecting mechanical properties), surface gloss and hardness, are among those obtainable.

However, there are five specific classes of polyester resins which have been developed with widely divergent properties to satisfy the performance requirements of the fields in which they are called upon to serve as components of RP. These five resin types have individually evolved from the best-known combinations of resin ingredients (Table II-11), common to the desired qualities, as long as the solvent and the curing systems to be employed, and any of the handling and processing-improvement characteristics may be incorporated. The final class of resin-type performance are not functions of resin type, but high heat-deflection temperatures may also show superior chemical durability.

Brief descriptions of the five major classes follow:

General Purpose

These multipurpose resins make possible the good mechanical and mechanical properties for which polyesters are used, regardless of cure by the reinforcement. They may be either rigid or resilient, filled or unfilled, and are used for general, nonstructural, decorative molding items. They also possess average-to-good chemical resistance, and, of course, may be infinitely modified to suit the great variety of molding processes and curing cycles. They will show discoloration, loss of gloss, and their blooming upon weathering, have a maximum long-term peak, continuous-exposure temperature of 257°F. Excellent resistance to good and may be further improved by incorporating daily phthalate monomer, but cure time and amount of catalyst required are correspondingly increased.

Light-Stable and Weather-Resistant Resins

These resins are manufactured to possess high clarity and freedom from any other foreign matter (ASTM A 974 = 20 to 100). Low viscosity (11.4-40 poise) for rapid wet-out of reinforcement, rigidity and high modulus for rapid cure, and also high surface gloss and hardness. They usually contain a mixture of styrene and methacrylonitrile or methacrylate-also monomers to provide freedom from surface

erosion and fiber blooming on weathering, and also contain stabilizers to resist yellowing or darkening due to action of ultraviolet rays in sunlight (phenyl salicylate and other hydroxybenzenes derivatives are typical stabilizers). Creation of a resin-rich surface layer provides good insurance against surface erosion and fiber blooming. Polyester gel coats prevent fiber erosion during long and continuous outdoor exposure, but are subject to cracking. Laminates made from transparent light-stable resins with standard approximately four years in a temperate climate (less in subtropical climates), prior to serious fiber blooming. The cured laminates may be rejuvenated with applications of clear lacquer. Recent developments have made possible application of a weather-resistant film on the laminate surfaces during manufacturing; the film remains an integral part of the laminate.

While not completely transparent, the light-stable and weather-resistant resins (Duro, Lantac) may be tinted and used in house or industrial structural glazing, as interior decorative panels. These panels are strong, light in weight, shatterproof, and are enjoying acceptance and increasing annual production as an outstanding application of RP.

Chemical-Resistant Polyester Resins

Utilization of chemical-resistant polyester resins to supersede metal structures which are invariably subject to rust and corrosion is only in its infancy. Large-scale structures (flume testing and hand lay-up) predominates (tanks, ducts, boats, piping, etc.), but high-temperature matched-to molded problems and pressure parts are also in wide usage.

The main cause of chemical attack of resins in aqueous environment is hydrolysis, which results in chemical decomposition due to attack and resultant rupture of the ester linkages in the polymer chain. Chemical-resistant resins have been designed so that ester linkages replace a percentage of the ester linkages by reacting fumaric acid and a high-boiling A-intermediate, and adding styrene monomer.

Establishment of more of a ring structure than that found in a general-purpose polyester resin. The higher molecular weight of such a resin also contributes to the resistance to hydrolysis.

Polyester resins with increased chemical durability and thermal stability, improved strength properties, which also permit blending with

higher proportions of styrene have resulted by varying isophthalic acid-based formulations to higher molecular weights.

Reference to chemical attack in polyesters has also been achieved by using hydroperoxide based A with maleic, fumaric, and phthalic acids and propylene glycol. The most chemical-resistant of a series of resins had a high heat-deflection temperature, low density, higher viscosity, absence of tack in curing, low curing shrinkage, and good adhesion to the glass reinforcement, all of which contributed to resistance to hydrolysis. A resin-rich surface also known resistance to chemical attack.

Chemical durability in polyester resins and cast-on laminates is evaluated by thermal shock within after exposure to determination of actual weight loss or gain, and also by determining the rate of resistance of physical properties. The extent of chemical durability depends upon the chemical to which exposure is made, and upon time of exposure. Extension of up to 60% of original strength in 20% acid concentrations and up to 80% in 6% strong-sulfuric concentrations is possible.

Resins with High Heat Deflection Temperature

The use of maleimide and triallyl cyanurate (potential bisoxazolones of 4 and 6, respectively) as comonomers with glycidium polyester (allyl) formulations has resulted in resins and house laminate structures with 50% retention of original strength when maintained and tested at 180°F. A stringent curing cycle is required, and the material is toxic and expensive. However, the 500°F limit coupled with ease of polyester handling provides a material which cannot be produced in any other way. Alternately, maleic anhydride conformances to demand materials which have the high strength, comparatively low modulus and dielectric properties of EP, yet which will withstand creep and thermal degradation at high temperatures.

Flame-Resistant Resins

These are also referred to as fire-resistant and self-extinguishing resins. Addition of chlorinated and unchlorinated acids, minimum amounts of monomer, and specific compounds such as antimony trioxide have enabled these resins, when made into structural panels, to gain very low flame-spread ratings (ASTM D635 and D747), and also values as low as 21 to 35

in the National Fire Underwriters' Tunnel Test. However, when subjected to the Columbia Fire Test¹ or equivalent, they generate great volumes of black smoke and carbon fumes. They are not self-extinguishing but burnable, which indicates the persistent limitations of the so-called self-extinguishing resins.

Large quantities of flame-resistant resins are used either for blending or full strength to reduce fire ratings to self-extinguishing for some building panels, electrical components and fuel tanks. However, the basic characteristics of being a combustible organic chemical precludes building codes approved as an interior construction material required to provide highest fireproof ratings. It also eliminates these materials from such uses as ablative shields.

The major markets or areas in which flame-resistant resins are essentially used² are of low-cost (1) aircraft and missiles (2) appliances (3) boats (4) construction (5) consumer products (6) containers (7) tanks and drums (8) electrical (9) film tanks and drums (10) transportation, and (11) reinforcement. Polymerization of some represent the largest resin markets for EP with phenolics and epoxide resin systems for EP with epoxy resin being included into the construction applications.

Rigid polyesters with flame retardation in which the material is permitted to be used at room temperatures directly from the manufacturer. The only requirement is that a base formulation be high enough in density at room temperature to provide strength and adequate strength after the resin has been polymerized. Adhesives (1 to 1.5%) are made to prevent this blocking.

Actually, any resin composition exhibiting a viscosity requirement may be marketed as a powdered polyester. Common-purpose and flame-retardant types are made by varying the major application is as a binder material for fiber-glass chopped-strand and other cast products. The suitability of the base resin in systems is particularly important in these binder resins. Most products which are to be used for hand lay-up and corrugated sheet manufacturing require fast wet-out and rapid absorption of the binder material in the laminating resin, while those for matched-on molding processes require a low-shrinkage binder which reduces warping and requires catalysts.

Molding compound formulations and some

proving operations may be built around use of powdered polyesters. Both acid resins are used in other proper processes from means of cross-linking resins.

APPENDIX D-1.1: SFI PROCEDURE FOR RUNNING EXOTHERM CURVES—POLYESTER RESINS

1. Scope

This method is designated for use in determining the "exotherm curve" of an uncured polyester resin, and covers the "Standard 1877 Exotherm Curve," and other standard exotherm curves, and certain variations which may be required for special resins or to supply information which is important for specific applications.

2. Test Sample

Liquid, uncured, unsaturated polyester resin, as available at room temperature. A minimum of 20 grams of resin is required for both exotherm curve and catalyzed stability; 30 grams of resin will suffice for the exotherm curve only.

3. Apparatus and Materials

- Recording Precursor³ 0 to 500°F range from 0.001 to 0.005 inches per hour chart speed.
- Constant-temperature water bath, controlled to 187°F ± 0.5°F, water capacity = 5 gallons, stirrer agitator, provided with rack to hold test tubes immersed in the water to within one-half inch of the top of the test tube.
- New, clean test tubes, soft glass with 16, 18 × 150 mm.
- Iron Contentation vials, M B & S gauge.
- Triple-beam scale with capacity of at least 100 g and readability of 0.01 gram.
- Yielded-weight stoppers for test tubes.
- 4-cmones for (wide mouth), spacers, test tube rack, plates.

4. Procedure

- Preparation of Catalyst Bath. Weigh 0.80 grams of benzoyl peroxide (99% purified into a 4-cmone, wide-mouth jar. Add 50 grams of the resin to be tested and mix thoroughly. Be careful to mix as little air as possible into the resin. Four 10 (±) gram into each of two of the 18 × 150 mm test tubes. Insert cork stoppers and let stand for 30 (±10) minutes away from heat and stirring. The remaining resin may be used for the exotherm curve (see Figure 1) or for catalyzed stability test.

¹ Leads & Northrup Spanderson (Type G) with chart \$300, or equivalent.
² Kinble 0550 Class 3, or equivalent.
³ Material is commercially available.

b) Preparation of Thermocouple The thermocouple should be long enough to reach easily from the bottom of the test tube to the bottom of the bath. The test tube when it is in place in the bath. The wires must be clean and free of kinks. Straighten the wires, and patch the ends with epoxy cloth if they are not bright. Field the ends in a pair of pliers so that they protrude together, in the same direction, about one inch.

With holding the wires firmly in the pliers, spread the ends apart and twist them together with the largest ten finger (five pairs) turns to form a tight braid, leaving the twisted portion in the part of the thermocouple which actually measures the temperature of the sample and to get a good curve there must be good, tight contact between the two wires in the bath, and the wires must be located in the center of the resin sample. If the two wires touch each other at any point other than at the twisted part (either above or below) the curve will not be correct. Bend the wires above and below the bath so that when the thermocouple (twisted portion) is inserted into the resin sample, the ends of the wires will be held to the center of the tube. Do not let these ends touch each other. (See Figure D-1.1.)

c) Running the Curve

When 25 (±10) minutes have elapsed from the time the resin was catalyzed, slide the twisted thermocouple wire into one of the test tubes containing 10 grams of catalyzed resin, so that the thermocouple is centered in the resin sample in all directions. Insert the test tube in the rack as far as it will go. Start the recording Precursor. Observe the exotherm curve that they are not touching each other anywhere except at the twisted portion. Let the recorder run for at least two minutes after the curve reaches its peak. Remove the tube from the bath, the plug from the tube and cut the wires just above the plug. Observe the plug for characteristics such as blooming (bubbles), transparency, unusual color, etc. If normal, discard plug and tube.

Run curves in duplicate. If they do not agree, run enough additional curves to produce reliable results.

GENCO CATALYTIC PROMOTERS

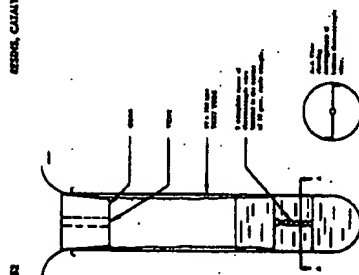


Figure 12-1: Sketch of thermocouple in test tube.

B. Report

Measure and record the following information from these curves which are considered reliable.

- Time from 1077 to bath temperature.
- Time from 1077 to 1077 above bath temperature.
- Peak temperature.

6. Variations

- Bath temperature and fluid: test may specify a different bath temperature and/or fluid (1077, room temperature, etc., all etc.) Test may specify bath temperature and fluid (1077, room temperature, etc., all etc.) Test may specify bath temperature and fluid (1077, room temperature, etc., all etc.) Test may specify bath temperature and fluid (1077, room temperature, etc., all etc.)
- Catalyst: Test may specify different catalyst and/or a different catalyst concentration.

Report on Company's Bulletin 712 or equivalent (See page 1077).

References

- | No. | Author(s) | Title or Periodic | Vol. | P. Act. | Year |
|-----|---|--|------|--------------------|---------------|
| 1 | Mitchell, J. J.,
Edith, L. M.,
Brenner, R. R.,
Winkler, A. | "Organic Chemistry," Vol. 1, New York, Interscience Publishers, Inc. | — | 11 | 1953 |
| 2 | Lawson, O. D. | Research Report No. 15, Purdue University, Lafayette, Ind. | — | — | Nov. 15, 1953 |
| 3 | Ann. | SP1-B.P. Dir. Proprietary | 16 | Follows in company | 1951 |

PATENTS 1953

No.	Author(s)	Title or Periodic	Vol.	P. Act.	Year
4	Bjorkstrom, J.	SP1-B.P. Dir. Proprietary	13	1-A	1953
5	Johnson, O. B., Mander, A. L., Porter, C. F.	SP1-B.P. Dir. Proprietary	14	17-A	1953
6	Ann, R. A.	SP1-B.P. Dir. Proprietary	15	1-A	1953
7	Edith, L.	SP1-B.P. Dir. Proprietary	13	15-A	1953
8	Levy, J. R., Smith, A. L.	SP1-B.P. Dir. Proprietary	11	17-C	1953
9	Morgan, P. A.	"Glass Reinforced Plastic," London, Ellis & Sons, Ltd.	—	28, 41	1957
10	Lawson, J.	"Polyester Resins," New York, Reinhold Publishing Corp.	—	—	1950
11	Bjorkstrom, J. et al.	"Polyesters and Their Applications," New York, Reinhold Publishing Corp.	—	—	1955
12	Nath, R. G.	WADO Rev. of Structural Plastics	—	1	Sept., 1959
13	Burns, R. B., Bourne, C. F., Owen, R. A.	"Polyester Resin Materials Study," Minnesota Chemical Co.	—	—	Early, Jan. 19, 1959
14	Ann, R. A., Guthrie, T. F. and Ann, R. W.	Modern Plastics	29 (Oct. 7)	14	1953
15	Ann.	"Composition and Utilization of Polyesters," Allied Chemical Corp.	—	25	1954
16	Edith, R. H.	General Electric Co.	—	—	1957
17	Lawson, J. R.	Personal Communication, Gild. Ann Co.	—	—	July 16, 1959
18	Atlas, S. M., Mark, H. F.	Intern. Ed. & Technol. Prototype	44	—	1951
19	Guthrie, S.	"Polyester and Resins," Princeton, N. J., D. Van Nostrand Co.	—	23	1959
20	Burns, R. B., Ann, R. A.	Ind. & Eng. Chem.	46, No. 8	1519	1954
21	Rockwell, T. R., Brown, C. A., Foster, S. S., Essential, I.	Ind. & Eng. Chem.	46, No. 8	1643	1954
22	Edith, R. W.	Ind. & Eng. Chem.	46, No. 8	1615	1954
23	Sims, C. B.	Private Communication, Pittsburgh Glass Co.	—	—	Apr. 5, 1959
24	Edith, G. M.	"Analytical Chemistry of Polyesters, Part I," "Monomers," Acrylic Resins, New York, Reinhold Publishing Corp.	15	649	1959
25	Edith	"Monomers," Acrylic Resins, New York, Reinhold Publishing Corp.	—	—	1954
26	Steen, M. C., Ann.	SP1-B.P. Dir. Proprietary	—	—	Oct., 1950

TABLE II-3.1. Phenolic Resin Types

Classification	Chemical Composition	Physical Properties
Condensation resins	Phenol + 1.0 to 1.5 formaldehyde = 0.5 to 1.0 resin	Phenol + 1.0 to 1.5 formaldehyde = 0.5 to 1.0 resin
Reaction catalyst	Strong bases, i.e., NaOH, KOH, Na ₂ CO ₃ , secondary amines, quaternary ammonium compounds, and combinations; quantity required = 0.1 to 0.5% of phenol charge. Catalysts are used with or without an external acid in some cases.	Weak bases, i.e., NH ₃ , primary, secondary, and tertiary amines; quantity required = 0.1 to 0.5% of phenol charge.
Method of handling and characteristics of the resin	Removed from reactor and cooled; maintained as a liquid.	Condensation water removed; removed from reactor and cooled; dissolved in alcohol for most uses.
General properties (increased data)	Water-soluble; viscosity = 100 to 1000 cP; pour point = 100 to 150°C; sp. gr. = 1.05 to 1.15; solids are thermosetting.	Slightly soluble in water; viscosity = 100 to 1000 cP; pour point = 100 to 150°C; sp. gr. = 1.05 to 1.15; solids are thermosetting.
Stability	Unstable; must be refrigerated prior to use to delay advance of the polymerization process.	Stable; some compositions have maximum shelf life of one week at 20°C.
Curing requirements and behavior	Cures by heat or change of pH or both; solids catalysts may be added.	Requires addition of 10-15% benzointhylphenol resin, formaldehyde, or other methylol-group donor to bring methylol value up to that of resins for cure; becomes thermosetting upon application of heat and high pressure.
Typical use	Blends, coatings and casting.	Industrial and decorative laminates, adhesives.

Chapter II-3

PHENOL-FORMALDEHYDE RESINS

Although the reaction between phenols and formaldehyde has been known since 1872, the chemist Leo Baekeland, through the period 1900-1909, systematically combined the reactants on an experimental mole basis and actually became the first to establish commercial uses for the phenol-formaldehyde resinous product.

Baekeland solved the then major problem of evolution of volatiles during cure by introducing pressure cooking. He also compounded the original phenolic molding compounds by adding fillers to phenolic resins to reduce their brittleness after molding. He prepared and laid the groundwork for the present Reinforced Plastics industry by using phenolic resins in liquid form to impregnate paper and fabric, which were dried and ultimately press-cured, making possible both industrial and decorative laminates.

Furthermore, the development of phenol-formaldehyde resin technology co-dated the expanding use of electric power in America. Because of their desirable electrical insulating properties and ease of molding, phenolics were placed in service to satisfy numerous industrial and domestic electrical requirements.

(1) Phenol-formaldehyde and catalyst are charged and the mix temperature raised to 140 to 160°C accompanied by adequate agitation. Resins remain as a continuous phase during reaction, while novolaks separate into two phases between which contact must be maintained by the agitation.

(2) Exothermic heat is generated when the reaction gets under way, and must be dissipated by refluxing under vacuum or by cooling-water coils inside the kettle.

(3) The reaction is carried to the stage at which from 50 to as much as 99% of the formaldehyde has been converted. This is determined by continually testing for free formaldehyde (see appendix to this chapter). The amount of free formaldehyde allowed to remain is governed by the contemplated end use. Volatility is also controlled by the degree of reaction and increases as polymerization progresses.

(4) Water is removed by vacuum distillation (40-60°C) from the reaction to which should be added and from the novolaks which are to become solid resins and in which swelling points must be controlled. These latter resins must be as free as possible of volatiles. Water is

PHENOL-FORMALDEHYDE RESIN MANUFACTURE

MANUFACTURE

Essentially, any of the compounds classed as phenols may be reacted with any aldehyde to yield a resin of the phenol-formaldehyde type (also known as phenoplasts or phenoplasts). However, phenol (C₆H₅O) also carboxylic acid, phenylacetic acid, or hydroxybenzoic acid, and formaldehyde (HCHO), also carboxylic acids, formalin, or formaldehyde, constitute respectively 75 and 90% of all present phenolic synthetic resin production. Phenol is commercially desirable because of its high purity and lower cost, and

generally permitted to remain in the storage tank, but the total amount of residual water is varied depending upon the end-use requirements.

(6) Liquid resins are cooled and pumped to storage or shipping containers. The sorbents are dropped to sediments in pans or onto a clean floor. They must be cooled rapidly to retain the melting point at the determined value, and are broken up into either pulverized, flaked, granulated, or other solid forms. To produce liquid sorbent resins, reaction products are redissolved in alcohol or other solvent prior to removal from the kettle.

Note: The condensation reaction is brought to completion as possible in the kettle preceding. To prevent further advances of cross-linking prior to ultimate use, one-step phenolics must be refrigerated, but two-step phenolics will exist at room temperature. The latter are characterized by a probably slight exotherm occurs as the ultimate rigid condensation polymer is formed.

A normal phenolic batch reaction requires from four to twelve hours for completion. Processes variations consist of reacting in pressure vessels or by a continuous process, making possible greatly reduced reaction time. These variations are suitable only to specific resin types, however.

The chemistry of phenol-formaldehyde resins is described as (a) little understood and (b) as a complex combination of condensation and addition polymerizations and rearrangement of groups, all of which may occur simultaneously. Excellent surveys of these reactions have been published, nevertheless, and these may be summarized as follows:

In formation of resins, the steps which occur in order are:

- (1) Methylation, or entry of methyl (CH₃) groups into the phenol ring in the ortho or para positions.
- (2) Condensation of two methyl groups to form an ether bridge.
- (3) Condensation between a methyl group and a phenol nucleus to form a methylene bridge (—CH₂—).
- (4) Decomposition of ether bridges (—O—) to form methylene bridges and formaldehyde, which immediately reacts via the first three reactions.

In the case of two-step resins:

(1) One molecule of formaldehyde plus two phenol nuclei will condense to form a methylene bridge (again in ortho or para positions) with elimination of water.

(2) In order to cure the sorbent, which as is permanently fusible (thermoplastic), it must be further reacted with a catalyst such as benzothiazotriazine or formaldehyde. These furnish additional methylene bridges so that the sorbent ultimately becomes a rigid cross-linked thermoset via the final process described for resins.

The physicochemical state of phenolic resins during cure may be further described by defining three distinct processes:

A-Stage resin (resin): The initial condensation product (see cross-linking).

B-Stage resin (resin): Cross-linking has commenced and the resin is thermoplastic, softening when hot and remaining hard and brittle at room temperature.

C-stage resin (resin): The final polymerization stage has been reached and the resin is completely thermoset (fusible and brittle).

Substitutions and Modifications

The many combinations of phenol and formaldehyde with various catalysts and curing conditions make possible a wide range of property variations in the finished thermoset resins. However, many substitutions are possible that improve the resins or eliminate undesirable properties.

A large number of phenol-related materials can be directly substituted for phenol. The property variation induced depends upon functionality, side-chain length, and other factors. A high degree of reactivity is desirable, as exemplified for instance by diphenyl acid which possesses eight reactive sites.

Commercial substitutes for formaldehyde are limited to paraformaldehyde and furfural (see Chapter II-4), but, as stated, formaldehyde is used in 95% of all phenolics produced.

Modifications include variations in batch cycle as well as changes in mole ratio, catalyst type and concentration. Equally important, however, are the complex and simple inorganic or organic compounds added to the batch to induce improvements in moisture or chemical resistance, flexibility or other specific properties. These modifiers represent a group whose effects are determined empirically, usually without prediction.

(4) Phenolics may be specially formulated so as to provide excellent flame resistance, for superior to that for polyesters.

(5) They exhibit good mechanical properties, and good chemical and moisture resistance.

(6) They may be cured by heat and pressure alone and do not require complex inhibitors, promoter and catalyst additions.

(7) Flexibility in water or water and alcohol of some phenolic types permits simplified handling.

(8) Phenolic resins have high heat-strength, minimizing tendency for warpage upon removal from molds.

(9) Cured phenolic resin solids are lower in specific gravity than those for polyester resins.

Disadvantages

(1) Phenolics have limited qualities of extreme brittleness. Attempts to plasticize phenolics (as with water-soluble glycols) to build in resiliency equivalent to that obtainable in polyester resins in degradation of cured properties.

(2) Other problems are had with phenolics. If the dark brown color of phenolics is avoided by processing in acid bathes rather than iron or steel, the brown color develops on curing, probably due to quinoids and chromophores which result from oxidation. Phenolics cannot compete advantageously with polyester, melamine, or urea resins.

(3) Phenolics require higher pressures for cure in almost all molding or laminating operations due to necessity of countering forces caused by escaping volatiles. Only phenolic-glass laminates are molded at lower pressures.

(4) Phenolics cure at a slower rate than polyesters. Only finished resins to which acid is added or resorcinol-formaldehyde resins will cure at room temperature, and these require further processing at elevated temperatures to develop ultimate properties.

(5) Phenolics must be stored at temperatures below room temperature, and have maximum shelf lives of approximately 90 days (liquid). Prolonged two-step resins to which benzothiazotriazine has been added may be maintained at room temperature for extended periods, but tend to agglomerate to some extent.

(6) Upon outdoor weathering, phenolic-glass laminates warp, leak, and darken further. However, during weathering they erode less than polyester resins.

terminated here, and their identification is in most instances left confidential and proprietary.

To further provide interesting property variations, blends (alloys), and mixtures of phenolic resins with other polymer types must be made and rubber (both thermoplastic and thermoplastic) have been made. These have made possible improved adhesion of resins to various substrates or reinforcements, and also have produced compounds with greater abrasion and wear resistance.

TESTING

In addition to tests for water (or solids) content (titration or dehydration methods), viscosity, specific gravity, etc. commonly used or described previously (Chapter II-1), several other tests which are especially applicable to phenolics have been devised. These comprise the following: two formaldehyde, nonvolatile matter (wax), stable cure, set time, water solubility (or tolerance). Procedures for these tests are duplicated in Appendices II-3.1 to II-3.6 at the end of this chapter.

PHENOLICS AS REINFORCED PLASTICS

Phenolic resins find application as adhesives, bonding and impregnating agents, molding compounds and laminates, in coating operations, and as products. The bonding, molding compound and laminating applications are of essential importance as Reinforced Plastics and will be discussed in detail.

In the general handling and curing, and in consideration of cured properties, certain advantages and disadvantages of phenolics compared to polyesters present themselves. These may be summarized as follows:

- Advantages**
- (1) Phenolics may be B-staged, permitting delayed cures. Only the more expensive DAP polyesters may be B-staged.
 - (2) General-purpose phenolics are 10 to 35% cheaper than polyesters on a solid basis.
 - (3) Phenolics possess higher temperatures per pound than polyesters, and retain a higher percentage of original strength after long-term high-temperature exposure.

Bending

Plastic resin has been used as a binder for fiber-glass and mineral wool insulation batts for many years. A strong-base type resin is usually used by mixing into a water-based formulation together with strongly alkaline curatives and stabilizers. The formulated resinous binder is spray-applied onto glass or wool fiber immediately after forming. The impregnated wool is collected on a moving belt which passes through a circulating air oven in which the resin is advanced through the B-stage and ultimately cured. Oven temperatures range from 225 to 450°F and the time required for curing depends upon the density and thickness of the mat to be produced. Cavity products are industrial resins (see Section III), fast-cure wood (phenolic-formaldehyde), and compressed, higher-density densified and insulation board.

Production of the compressed insulation board employs a unique process adaptation in which fiber-glass insulation-type matting with plastic resin applied passes through the forming stage only, and is rolled up prior to curing the resin. Hence, the resin remains in the B-stage and two or three months' shelf life is normal if storage in excess of room temperature is avoided.

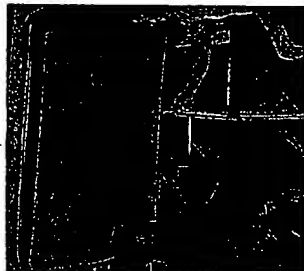


Figure 12-41. Insulation of automotive head-liner made from phenolic-bonded compressed fiber-glass insulation board. (Courtesy American M-Core Corporation and Johns-Manville Fiber Glass Division)

The compressed board is ultimately processed to a finished product by molding to predetermined thickness steps as a laminate in a heated flat-plate or combined press mold. Density after molding varies from five to ten pounds per cubic foot as compared to maximum densities of only three pounds per cubic foot for the fiber-glass wool and fifteen pounds for mineral wool insulation.

Molding temperatures are maintained in the vicinity of 450°F so that more rapid cures are possible. Distillation of the resin is minimized due to the closed mold.

Originally (1931) the cured compressed board was channeled into products which utilized its properties of resiliency and vibration damping. Five-inch diameter rocket burner stop and automotive protective dash panels were manufactured in quantity during the period 1931 to 1934. Subsequently, concentrated development resulted in a composite panel consisting of a decorative fiber glass fabric applied to the compressed board. Both the fabric and the B-stage resin-wood combination are laid up and cured together in a combined press mold. A thin film of thermoplastic material is interlaminated and carbon during the molding cycle, bonding the glass fabric to the surface of the compressed board.

A unitized, one-piece automotive head-liner and a decorative acoustical ceiling panel represent the first major-volume items utilizing the compressed-board process. Figures 12-42 and 12-43 illustrate, respectively, the automotive head-liner and the acoustical ceiling panel. Sound-damping qualities of the ceiling panel compared with other standard acoustical ceiling 58 may be estimated by testing that the fiber-glass compressed board provides equivalent sound absorption, yet it weighs only one-fourth as much as standard panels.

Additional applications involving the bonding characteristics of plastic resin comprise use in structural, fireproof materials, laundry acid cures and mold, impregnant for fiber-glass mat used in battery separator, and other miscellaneous uses.

Molding Compounds

In the present state of the art, resin monomers or intermediate processors supply, ready to mold, the major portion of all plastic molding compounds used. The compounds are delivered to the molder in any of the four follow-

ing forms: granular powders, random reinforced fibers (rochels), chopped or uncutted resin-coated fabric, and resin plus fibers plasticized with solvents.

Shrinkage or difference between room-temperature dimensions of a mold and the article molded therefrom is another parameter governing successful molding, and is measurable by ASTM Method D305.

Rate of cure is an additional property requiring control, and information is generally supplied by the compound manufacturer (see Appendix II-2.4).

Special compounds require changing at a mold temperature of 170°F and subsequent increase to 350°F, with a 20 to 30-minute cycle. These are designed for superior derived-temperature strength properties and abrasion resistance.

Old pressure molding to form a part, followed by oven curing, conditions an original molding method still in use. Molded articles have poorer surface, lower impact, and higher water absorption than hot-molded articles, and are slightly lower in mechanical strength.

Common fillers and reinforcements for molding compounds are wood, metallic, steel, mica, clay, asbestos, graphite, nylon, rubber, glass,

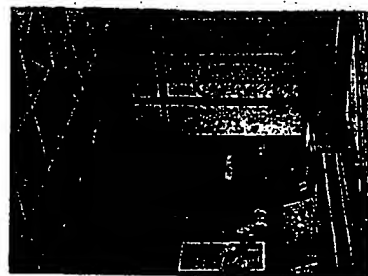


Figure 12-42. Acoustical ceiling panels made from phenolic-bonded compressed fiber-glass insulation board. (Courtesy Johns-Manville Fiber Glass Division)

ing forms: granular powders, random reinforced fibers (rochels), chopped or uncutted resin-coated fabric, and resin plus fibers plasticized with solvents.

Shrinkage or difference between room-temperature dimensions of a mold and the article molded therefrom is another parameter governing successful molding, and is measurable by ASTM Method D305.

Rate of cure is an additional property requiring control, and information is generally supplied by the compound manufacturer (see Appendix II-2.4).

Special compounds require changing at a mold temperature of 170°F and subsequent increase to 350°F, with a 20 to 30-minute cycle. These are designed for superior derived-temperature strength properties and abrasion resistance.

Old pressure molding to form a part, followed by oven curing, conditions an original molding method still in use. Molded articles have poorer surface, lower impact, and higher water absorption than hot-molded articles, and are slightly lower in mechanical strength.

Common fillers and reinforcements for molding compounds are wood, metallic, steel, mica, clay, asbestos, graphite, nylon, rubber, glass,

ing compounds can be led to the cavity as molding compound may be supplied by a vibrator. Random fiber or uncutted cloth types may be preformed roughly by hand or by a vibrating or piling machine. Transfer molding usually requires a preformed slug, with up to several unit-sized slugs placed in the transfer pot to mold a large-sized item.

Preheating, if practicable and controllable, may effectively reduce the required time for molding.

Molding temperatures vary between 370 and 450°F. Molding pressures up to 5000 psi are required and are usually determined by the nature of the mold and the type of compound. By predetermined plasticity of the compound, the plasticity of "flow" of a molding compound is also very important in determining whether the compound will properly fill all sections of the mold during the press cycle.

ASTM Method D305 has been proposed to specify an index of this "flow" factor. ASTM mold- ing factors of 200 for extremely soft (high-flow) materials (500 psi minimum pressure required) to 50,000 (or very hard (low-flow) materials (5000 minimum pressure required) are determined by measuring pressure necessary to close a standard cup mold to a specified fir-

ing factors: granular powders, random reinforced fibers (rochels), chopped or uncutted resin-coated fabric, and resin plus fibers plasticized with solvents.

Shrinkage or difference between room-temperature dimensions of a mold and the article molded therefrom is another parameter governing successful molding, and is measurable by ASTM Method D305.

Rate of cure is an additional property requiring control, and information is generally supplied by the compound manufacturer (see Appendix II-2.4).

Special compounds require changing at a mold temperature of 170°F and subsequent increase to 350°F, with a 20 to 30-minute cycle. These are designed for superior derived-temperature strength properties and abrasion resistance.

Old pressure molding to form a part, followed by oven curing, conditions an original molding method still in use. Molded articles have poorer surface, lower impact, and higher water absorption than hot-molded articles, and are slightly lower in mechanical strength.

Common fillers and reinforcements for molding compounds are wood, metallic, steel, mica, clay, asbestos, graphite, nylon, rubber, glass,

A comparison of the properties of basis types (1) and (2) is given in Table II. The results are similar to those obtained by cutting to size and stacking follow. However, at this stage, the fabric may be rolled (interleaved) for later use as a prepreg material.

[illegible]^a 43 points of 80°C, based on 100% conversion.

Specific properties of phenolic-resin laminates may be determined by consulting references 12, 13, 14, 16, 17, Military Specification MIL-R-2098 outlines properties and performance requirements for phenolic low-pressure laminate resins. A comparison is made in Table I between some of the properties of the resin used in the construction of the aircraft fuselage and those of other available materials.

RESIN, CATALYST, PROMOTERS

44

Table II-2.3 of physical properties of laminates those made using the "Standard" general-purpose resin using a high-grade phenolic resin with poor rigid polymer.

TABLE II-2.3 TYPICAL PROPERTIES OF HIGH-GRADE PHENOLIC LAMINATING RESIN COMPARED TO THOSE FOR CHEMICAL-GRADATION RIGID POLYMER LAMINATE

	Phenolic Resin Viscosity (cP) at 25°C	Phenolic Resin Viscosity (cP) at 100°C	0.5 Rapid Polymer as One Step in 2-30 min
Plastic strength, psi (RT)	60,000	60,000	60,000
After 1 hr @ 800°F (tested at 800)	20,000	60,000	(Heat def. = 200°F)
Plastic modulus, psi	3.4 X 10 ⁶	4.0 X 10 ⁶	3.0 X 10 ⁶
Tensile strength, psi	60,000	60,000	60,000
Compressive strength, psi	60,000	60,000	60,000
Water absorption, %	2.5	0.10	0.10
Specific gravity	—	—	1.0
Heat content	—	—	25%

APPENDIX 0.2.1—PHENOLIC RESIN TESTS

TEST: FREE FORMALDEHYDE CONTENT OF PHENOLIC RESIN—HYDROXYLAMINE HYDROCHLORIDE METHOD

Applications of Test

1. This method is used to determine the free formaldehyde content of phenolic resins and formalin solutions to be used for the manufacture of phenolic resins.

Apparatus

- 1) Balances, accurate to 0.01 gram.
- 2) Beaker, 400 ml.
- 3) Buret, range 0-10 ml, graduated to 0.1 ml.
- 4) Graduated, 100 ml, graduated to 1.0 ml.
- 5) Magnesia stirrer.
- 6) pH meter.
- 7) Weighing bottle.

Reagents

- 1) 2N alcohol.
- 2) Aqueous hydroxylamine hydrochloride solution, 10%.
- 3) 1N standard sodium hydroxide solution.
- 4) 0.1 N sulfuric acid solution.

Procedure

- 1) Weigh a water-soluble resin (or use with heat chole).
- 2) Weigh into the beaker 10 grams of sample.
- 3) Dissolve the resin in 100 ml of distilled water.

- 1) Neutralize to a pH of 4, using the pH meter, and 0.1N sulfuric acid solution while stirring.
- 2) Add 40 ml of hydroxylamine hydrochloride solution.
- 3) Wait 5 minutes for a process sample and 20 minutes for a final sample then dilute with 1N sodium hydroxide solution to a pH of 4.4. Record the time. If more than 45 ml of time is used, reduce the sample size and repeat the above procedure.

4.1 Phenolic Resin

- 1) Weigh a 400-ml beaker to the nearest 0.01 gram.
- 2) Weigh into the beaker 10 grams of sample, to the nearest 0.01 gram, and dissolve in 100 ml of 2N alcohol and 20 ml of water.
- 3) Stir the mixture in Section 4.1, steps (1) through (3).

4.2 Phenolic Resin

- 1) Measure 100 ml of distilled water into a 400-ml beaker.
- 2) Weigh 3.00 ± 0.01 grams of sample into the beaker, by difference.
- 3) Dissolve by placing on a magnesia stirrer.
- 4) Follow the procedure in Section 4.1, steps (1) through (3).

4.3 Blank titre

- 1) Determine the blank titre on 40 ml of hydroxylamine hydrochloride solution

PHENOL-FORMALDEHYDE RESINS

45

by titrating to a pH of 4.0 with standard sodium hydroxide solution. For formalin blank titre, add 100 ml of water to the hydroxylamine hydrochloride.

Report

- 1) Report the per cent formaldehyde to the nearest 0.1%.

Calculations

- 1) Formaldehyde, per cent by wt.

APPENDIX 0.2.2—PHENOLIC RESIN TESTS

TEST: NONVOLATILE MATTER ("MECHANOL SOLIDS") IN WATER-SOLUBLE PHENOLIC RESINS

Applications of Test

1. This method is used to determine the quantity of nonvolatile matter present in water-soluble phenolic resin solutions under arbitrary test conditions. Methanol is used as a drying aid unless otherwise specified.

Apparatus

- 1) a) Thermometer, range 0-50°C, graduated to 1°C.
- b) Oven, gravity convection type, controlled to 1°C.
- c) Rapid weighing bottle.
- d) Drying dishes, stainless tin with metal cover, having an inside diameter of approximately 1 1/4 in. and a height of approximately 1 1/4 in.
- e) Desiccator.
- f) Balance, accurate to 0.0001 gram.

Reagents

- 1) a) Methanol, reagent grade, acetone-free.
- b) Anhydrous ethanol.
- c) 2N alcohol.

Procedure

- 1) a) Heat 3 drying dishes for at least 20 min. in the 100°C oven. Cool for at least 10 min. in a desiccator. Weigh each dish to the nearest 0.0001 gram. Place 10 ml of methanol, unless otherwise specified on each analysis sheet, into each dish. From the stoppered weighing bottle, weigh by difference to the nearest 0.0001 gram 1.0 to 1.1 gram of the resin solution into each drying dish.
- b) Dissolve the resin solution by a slight circular motion. Touch the pan bottom

lightly to a hot plate and swirl if difficultly in dissolving the resin. Remove the dishes such as to permit evaporation but prevent loss by splashing.

- 1) Within 30 minutes after preparation, place the partially covered drying dishes in the constant-temperature oven (Note 1a), to close proximity to the bath of the thermometer, and allow them to remain for a period of 1 hour ± 5 minutes (Note 7b).
- 2) At the end of the 1-hour heating period, remove the dishes to the desiccator and cool for 10 to 20 minutes at room temperature. Then weigh the drying dishes with the residues immediately to the nearest 0.0001 gram.

Calculations

- 1) Nonvolatile matter, per cent

$$= \frac{\text{wt. of residue}}{\text{wt. of sample}} \times 100$$

Report

- 1) Report per cent nonvolatile matter to the nearest 0.05% "methanol solids." List all these results.

Notes

- 1) a) In a gravity-type oven, which depends upon the natural circulation of air for uniformity of temperature, use only one shelf for supporting the specimens. Check all vents of the oven to be sure they are open.
- 2) Place only one set of solids in the oven at any given time. Solid sets may be inserted at 1-hour intervals, if necessary.

APPENDIX B-2.3—PHENOLIC RESIN TESTS

TEST: NONVOLATILE MATTER IN VARNISH PHENOLIC RESINS

Application of Test

1. This method is used to determine the non-volatile content of phenolic varnishes, based on an arbitrary set of conditions.

Apparatus

- a) Balance accurate to 0.001 gram.
- b) Drying dishes, stainless tin, having an inside diameter of approximately 3 1/2 inches and a height of approximately 1 1/2 inches. A standard pint tin can cover is suitable for this use.
- c) Desiccator.
- d) Oven, gravity convection, controlled at 120°C ± 1°C.
- e) Weighing bottle and stopper.
- f) Thermometer, range of 0 to 200°C, graduated to 1°C.

Calculation

- a) Non-volatile matter,

$$\% = \frac{(\text{wt. of matter} + \text{dish}) - (\text{wt. of dish})}{\text{wt. of sample}} \times 100$$

Report

1. Report the average of the three determinations to the nearest 0.05%. Do not use results more than 0.05% apart. At least two results are to be used in the report.

APPENDIX B-2.4—PHENOLIC RESIN TESTS

TEST: DILUTABILITY OF WATER-SOLUBLE PHENOLIC RESINS—STANDARD METHOD

Application of Test

1. This test is used to determine the tolerance of water-soluble phenolic resins for water, without producing turbidity.

Apparatus

- a) Rubber, 600 ml.
- b) Graduated, range 50 ml, with glass stopper, graduated to 2 ml.
- c) Graduated, range 10 ml, graduated to 0.2 ml.
- d) Constant temperature bath, controlled at 25°C ± 0.5°C.

Procedure

1. Fill a 600-ml beaker with water and maintain this water at a temperature of 25°C ±

APPENDIX B-2.5—PHENOLIC RESIN TESTS

TEST: STROKER CURE OF PHENOLIC RESINS, HOT-PLATE METHOD

Application of Test

1. This method is used to determine the curing time of thermosetting resins.

Apparatus

- a) Refrigeration upon, bowl 1/4 inch deep and 1 1/2 inch in diameter.
- b) Hot plate, 4 inch x 6 inch surface enclosed at 150 ± 0.5°C.
- c) Thermometer, range 0 to 200°C, graduated to 1°C.
- d) Specimen, metal, 4 inch.
- e) Therm, accurate to 1 second.

Procedure

1. Set up the hot plate in an area shielded from drafts.
2. Coat the hot plate with a thin film of specimen var. Wipe off any excess that may remain. The var will make removal of the cured resin easier after the test is completed.
3. Adjust the hot plate to 150 ± 0.5°C. Stir the resin thoroughly and, using the designated spoon, place a small amount of the resin in the center of the hot plate. At the same time, start the stopwatch and spread the resin with a circular motion of

APPENDIX B-2.5—PHENOLIC RESIN TESTS

TEST: STROKER CURE OF PHENOLIC RESINS, HOT-PLATE METHOD

Application of Test

1. This method is used to determine the curing time of thermosetting resins.

Apparatus

- a) Refrigeration upon, bowl 1/4 inch deep and 1 1/2 inch in diameter.
- b) Hot plate, 4 inch x 6 inch surface enclosed at 150 ± 0.5°C.
- c) Thermometer, range 0 to 200°C, graduated to 1°C.
- d) Specimen, metal, 4 inch.
- e) Therm, accurate to 1 second.

Procedure

1. Set up the hot plate in an area shielded from drafts.
2. Coat the hot plate with a thin film of specimen var. Wipe off any excess that may remain. The var will make removal of the cured resin easier after the test is completed.
3. Adjust the hot plate to 150 ± 0.5°C. Stir the resin thoroughly and, using the designated spoon, place a small amount of the resin in the center of the hot plate. At the same time, start the stopwatch and spread the resin with a circular motion of

APPENDIX B-2.5—PHENOLIC RESIN TESTS

TEST: STROKER CURE OF PHENOLIC RESINS, HOT-PLATE METHOD

Application of Test

1. This method is used to determine the curing time of thermosetting resins.

Apparatus

- a) Refrigeration upon, bowl 1/4 inch deep and 1 1/2 inch in diameter.
- b) Hot plate, 4 inch x 6 inch surface enclosed at 150 ± 0.5°C.
- c) Thermometer, range 0 to 200°C, graduated to 1°C.
- d) Specimen, metal, 4 inch.
- e) Therm, accurate to 1 second.

Procedure

1. Set up the hot plate in an area shielded from drafts.
2. Coat the hot plate with a thin film of specimen var. Wipe off any excess that may remain. The var will make removal of the cured resin easier after the test is completed.
3. Adjust the hot plate to 150 ± 0.5°C. Stir the resin thoroughly and, using the designated spoon, place a small amount of the resin in the center of the hot plate. At the same time, start the stopwatch and spread the resin with a circular motion of

APPENDIX D.2.6—PHENOLIC RESIN TESTS

TEST: SET TIME OF PHENOLIC VARNISHES

Applications of Test

1. This method is used to determine the relative rate of polymerization of varnishes at a given temperature.

Apparatus

- a) Agitator, a 15-inch length of 8-mm glass rod sealed to a 6-cm length of 9-mm glass rod.
- b) Balance, accurate to 0.01 gram.
- c) Constant temperature bath, controlled at 40°C ± 1°C.
- d) Laboratory motor, 350 rpm, with clutch to fit 8-mm rod.
- e) Test tubes, Pyrex, 100 mm × 20 mm.
- f) Test tube clamp.
- g) Timer, accurate to 0.1 second.

Procedure

1. a) Attach the glass-rod agitator to the bottom of the laboratory motor. Weigh, to the nearest 0.1 gram, 2.4 to 2.6 gm of the resin sample into a test tube. Slip the constant temperature bath over the test tube. Lift the test tube, slip the agitator between the test tube and the bath. Center the agitator in the test tube. Then clamp the test tube into this position tightly.

Report

2. a) Attach the glass-rod agitator to the bottom of the laboratory motor. Weigh, to the nearest 0.1 gram, 2.4 to 2.6 gm of the resin sample into a test tube. Slip the constant temperature bath over the test tube. Lift the test tube, slip the agitator between the test tube and the bath. Center the agitator in the test tube. Then clamp the test tube into this position tightly.

Notes

3. In some cases, transfer of the resin to the agitator is not complete. The change from liquid to an amber, gel-like solid and the resulting agitator still held true and are the best means to detect the end point.

References

No.	Author(s)	Title or Publication	Vol.	P. No.	Year
1	Ellis, G. M., ed.	Analytical Chemistry of Polymers, Part 1, New York: Interscience Publishers, Inc.	—	27	1959
2	Richter, J.	Polymers and Their Applications, New York: Reinhold Publishing Corp.	—	104	1959
3	Haack, D. M., Jr.	"Development of Fabrication Techniques for High-Temperature Resistant Structural Composites," SPI-2.P. Div. Preprint	3	34	1953
4	White, R. B.	"Glass Frits Molding," SPI-2.P. Div. Preprint	9	110	1954
5	Morgan, P. A.	Glass Reinforced Plastics; Ulf, 2nd Ed.	—	—	1957
6	Shand, E. B.	Glass Engineering Handbook; New York: McGraw-Hill Book Co., Inc.	—	—	1955

PHENOL-RESOL-EPICLORIC RESINS

No.	Author(s)	Title or Publication	Vol.	P. No.	Year
7	Burke, E. H. Landy, R. J.	"Colophony Plastics for Use in Rocket Motors," SPI-2.P. Div. Preprint	10	102	1961
8	Olsen, J. J.	"Comparison Phenolic and Poly-ester Resin Materials," SPI-2.P. Div. Preprint	13	94	1958
9	Gould, D. P.	"Phenolic Resins," New York: Reinhold Publishing Corp.	—	—	1959
10	Asoc.	NEMA Standard LP-1 for Industrial Laminated Thermosetting Products	May	—	1959
11	Asoc.	NEMA Standard LP-3 for Laminated Thermosetting Densitometric Resins	May	—	1957
12	Asoc.	Technical Bulletin, Taylor Fibre Co.	—	—	1961
13	Baker, E. E.	"Fading Properties of Various Glass-Fiber Reinforced Plastic Laminates," WADCO Tech Report No. 59-39	—	—	1955
14	Worm, P. Hartsh, B. O.	"Weathering of Glass-Fiber-Reinforced Plastic Laminates," WADCO Tech. Report No. 59-318	—	—	1955
15	O'Brien, F. E. Ogden, S. J.	"Investigation of Thermal Properties of Plastic Laminates, Core and Sandwich Panel," WADCO Tech Report No. 59-320, Part 1 & 2	—	—	1957
16	Owen, G. M. Vandew, J. A. Hammann, W. F.	"Harvest and Room Temperature Properties of Plastic Laminates," WADCO Tech Report No. 59-374	—	—	1953
17	Asoc.	"Plastics for Flight Vehicles," AN-17 U.S. Forest Products Lab.	—	—	1950
18	Asoc.	Modern Plastics Encyclopedia	27	128	1961
19	Lensell, A. P. Mikawa, J. B. Asoc.	Modern Plastics Encyclopedia	28	246	1961
20	Golding, B.	Modern Plastics Encyclopedia	29	228	1962
21	Davis, A.	Modern Plastics Encyclopedia	30	242	1962
22	McCall, L.	Modern Plastics Encyclopedia	31	242	1962
23	Asoc.	Modern Plastics Encyclopedia	32	242	1962
24	Asoc.	Modern Plastics Encyclopedia	33	242	1962
25	Asoc.	Modern Plastics Encyclopedia	34	242	1962
26	Asoc.	Modern Plastics Encyclopedia	35	242	1962
27	Asoc.	Modern Plastics Encyclopedia	36	242	1962
28	Asoc.	Modern Plastics Encyclopedia	37	242	1962
29	Asoc.	Modern Plastics Encyclopedia	38	242	1962
30	Asoc.	Modern Plastics Encyclopedia	39	242	1962
31	Asoc.	Modern Plastics Encyclopedia	40	242	1962
32	Asoc.	Modern Plastics Encyclopedia	41	242	1962
33	Asoc.	Modern Plastics Encyclopedia	42	242	1962
34	Asoc.	Modern Plastics Encyclopedia	43	242	1962
35	Asoc.	Modern Plastics Encyclopedia	44	242	1962
36	Asoc.	Modern Plastics Encyclopedia	45	242	1962
37	Asoc.	Modern Plastics Encyclopedia	46	242	1962
38	Asoc.	Modern Plastics Encyclopedia	47	242	1962
39	Asoc.	Modern Plastics Encyclopedia	48	242	1962
40	Asoc.	Modern Plastics Encyclopedia	49	242	1962
41	Asoc.	Modern Plastics Encyclopedia	50	242	1962
42	Asoc.	Modern Plastics Encyclopedia	51	242	1962
43	Asoc.	Modern Plastics Encyclopedia	52	242	1962
44	Asoc.	Modern Plastics Encyclopedia	53	242	1962
45	Asoc.	Modern Plastics Encyclopedia	54	242	1962
46	Asoc.	Modern Plastics Encyclopedia	55	242	1962
47	Asoc.	Modern Plastics Encyclopedia	56	242	1962
48	Asoc.	Modern Plastics Encyclopedia	57	242	1962
49	Asoc.	Modern Plastics Encyclopedia	58	242	1962
50	Asoc.	Modern Plastics Encyclopedia	59	242	1962
51	Asoc.	Modern Plastics Encyclopedia	60	242	1962
52	Asoc.	Modern Plastics Encyclopedia	61	242	1962
53	Asoc.	Modern Plastics Encyclopedia	62	242	1962
54	Asoc.	Modern Plastics Encyclopedia	63	242	1962
55	Asoc.	Modern Plastics Encyclopedia	64	242	1962
56	Asoc.	Modern Plastics Encyclopedia	65	242	1962
57	Asoc.	Modern Plastics Encyclopedia	66	242	1962
58	Asoc.	Modern Plastics Encyclopedia	67	242	1962
59	Asoc.	Modern Plastics Encyclopedia	68	242	1962
60	Asoc.	Modern Plastics Encyclopedia	69	242	1962
61	Asoc.	Modern Plastics Encyclopedia	70	242	1962
62	Asoc.	Modern Plastics Encyclopedia	71	242	1962
63	Asoc.	Modern Plastics Encyclopedia	72	242	1962
64	Asoc.	Modern Plastics Encyclopedia	73	242	1962
65	Asoc.	Modern Plastics Encyclopedia	74	242	1962
66	Asoc.	Modern Plastics Encyclopedia	75	242	1962
67	Asoc.	Modern Plastics Encyclopedia	76	242	1962
68	Asoc.	Modern Plastics Encyclopedia	77	242	1962
69	Asoc.	Modern Plastics Encyclopedia	78	242	1962
70	Asoc.	Modern Plastics Encyclopedia	79	242	1962
71	Asoc.	Modern Plastics Encyclopedia	80	242	1962
72	Asoc.	Modern Plastics Encyclopedia	81	242	1962
73	Asoc.	Modern Plastics Encyclopedia	82	242	1962
74	Asoc.	Modern Plastics Encyclopedia	83	242	1962
75	Asoc.	Modern Plastics Encyclopedia	84	242	1962
76	Asoc.	Modern Plastics Encyclopedia	85	242	1962
77	Asoc.	Modern Plastics Encyclopedia	86	242	1962
78	Asoc.	Modern Plastics Encyclopedia	87	242	1962
79	Asoc.	Modern Plastics Encyclopedia	88	242	1962
80	Asoc.	Modern Plastics Encyclopedia	89	242	1962
81	Asoc.	Modern Plastics Encyclopedia	90	242	1962
82	Asoc.	Modern Plastics Encyclopedia	91	242	1962
83	Asoc.	Modern Plastics Encyclopedia	92	242	1962
84	Asoc.	Modern Plastics Encyclopedia	93	242	1962
85	Asoc.	Modern Plastics Encyclopedia	94	242	1962
86	Asoc.	Modern Plastics Encyclopedia	95	242	1962
87	Asoc.	Modern Plastics Encyclopedia	96	242	1962
88	Asoc.	Modern Plastics Encyclopedia	97	242	1962
89	Asoc.	Modern Plastics Encyclopedia	98	242	1962
90	Asoc.	Modern Plastics Encyclopedia	99	242	1962
91	Asoc.	Modern Plastics Encyclopedia	100	242	1962

Chapter II-3

EPOXY RESINS

INTRODUCTION AND DEFINITIONS

Epoxy resins are characterized by the presence of oxirane or epoxide groupings



These may be present in the raw materials used to form the resin (conventional or novolac type) or may be formed during the reaction (epoxidized polyolefins type). Reactive hydroxyl groups and vinyl unsaturation also appear in epoxide epoxy resin molecules.

Whether the case, aromatic or aliphatic polymer molecules containing an average of more than one of the epoxide groups comprise epoxy resins. The groups may occupy various positions within the molecule, such as terminal, internal, ring situated, glycidyl, etc.

Cure may be established using materials chosen as hardeners or curing agents. These react to polymerize epoxy resins through either one of two methods: (a) catalytic means in which the epoxide groups on the resin molecules interact (catalytic example—boron trifluoride), or (b) by cross-linking in which epoxidizing molecules unite with the epoxy resin molecules becoming part of the cured resin network (example—amine curing agents).^{1,2} In both cases, the epoxide groups are opened and subsequently a well-built polymer structure is formed. The three-membered epoxide ring is of interest due to its high reactivity potential, contributing to the fact that epoxy resins per se have exhibited interesting and superior cured properties. This is true primarily because, during cure, no rearrangement occurs in the backbone of the resin molecule, the reactive epoxide groups usually being held on the cured molecule as appendages.

Table II-3.1 presents a classified summary of

the three major types of epoxy resins of commercial significance: (a) epichlorohydrin-bisphenol A (conventional), (b) epoxy novolac, and (c) epoxidized polyolefin resins. Curing agent or hardener systems for the conventional epoxy are described and their properties and optimum reaction quantities summarized in Table II-3.1. Curing agents for the novolac and polyolefin epoxies are summarized in Table II-3.1.

The behavior and handling of epoxy resins will be clarified by noting the following definitions: *Epoxide Equivalent* represents the accepted method of expressing epoxy resin functionality, and is the weight in grams of the amount of resin which contains one gram-molecular equivalent of epoxy (usually determined by IEC reaction and titration, and supplied by the resin manufacturer). *Epoxy Value* is another expression of epoxy resin functionality, and is defined as the number of epoxy groups contained in 100 grams of resin. Epoxy value is equal to the epoxide equivalent divided into 100. In order to determine required resin and curing-agent combining quantities, the units equivalent is first determined by:

$$\begin{array}{l} \text{Molecular weight of the resin curing agent} \quad 0 \\ \text{Number of reactive hydrogen atoms} \quad \text{in the resin molecule} \quad 100 \\ \hline \text{The required amount of curing agent (Z phr)} \text{ is then determined by equating the ratio of:} \\ \text{epoxide equivalent to (Z phr)} \quad 0 \end{array}$$

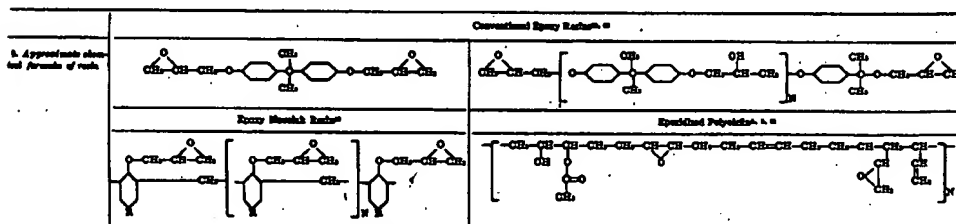
As an example, diethylene tetraamine, H₂N—CH₂—CH₂—NH₂, has a molecular weight of 103 and five reactive hydrogens are contained in the molecule, thus providing an amine equivalent of 103.1/5, or 20.7. Then, for a

Foot continued on p. 11.

70	Author(s)	Title or Subject	Vol.	P. No.	Year
24	Assoc.	"Recommended Practices for Fabricating Laminated Plastics," NEMA Publication No. 8-107 (part of print)	—	—	Dec., 1945
25	Brickman, W. O. Arlberg, W. E.	"Study of Various Reinforcing Materials in Polyester Resin Composites," EP1-R.P. Div. Preprint	13	17-C	1957
26	Sumner, S. E.	"A High-Temperature Structural Adhesive," EP1-R.P. Div. Preprint	9	7-1	1954
27	Quinn, P. E. Lynch, L. L.	"Free-Tech—A New Material for Greening Molding," EP1-R.P. Div. Preprint	17	2-D	1952
28	Assoc.	"High-Temperature Properties of Laminated Thermosetting Resins," NEMA Standards Publication 133	Aug.	—	1951
29	Assoc.	"Test for Flame Resistance of Laminated Sheets or Cast Laminating Materials," NEMA Standard Publication No. 360	Mar.	—	1951
30	Shultz, L.	"Survey of Recent Advances in Resins for Reinforced Plastics," EP1-R.P. Div. Preprint	13	13-A	1957
31	Morris, W.	"A Study of Cure in Decorative Laminates," TAPP1	43	—	July, 1959
32	Hansen, G. J.	Personal Communication (Glass Reinforced Plastic Fiber Glass Div.)	57	—	Mar. 29, 1953
33	Latham, M. E.	"Low-Pressure Densified Laminates," EP1-R.P. Div. Preprint	15	23	1950

TABLE II-1. CLASSIFICATION OF COMMERCIALLY SIGNIFICANT EPOXY RESIN TYPES

	Conventional Epoxy Resins ^a		Epoxy Novolac Resins ^b					Specified Polyethers ^{c, d, e}	
1. Chemical composition and/or description	Diglycidyl ether of bisphenol A with only smaller amounts of higher mol. wt. novolacs	High mol. wt. novolacs of diglycidyl ether of bisphenol A							
2. Epoxy resin materials	Epichlorohydrin, epichlorohydrin	Epichlorohydrin, epichlorohydrin, sodium carbonate	Novolac resins, epichlorohydrin					Oxide plus peroxide acid	
3. Molecular weight									
			Thermal Stability - Random Diglycidyl Ether						
	Actual (used in making resin) Theoretical (in cured resin)	1 (b) to 4 (b) (b) 1 (b) to 4 (b) (b)							
4. Reaction catalyst	NaOH (2 molar/100 parts bisphenol A) or other catalyst used to neutralize the HCl which is formed.	NaOH (2 molar/100 parts bisphenol A) or other catalyst used to neutralize the HCl which is formed.						In-situ novolac resin	
5. Reaction procedure	Epichlorohydrin and epichlorohydrin solution are stirred together at 100°F (approx) to 150°F (approx). NaOH solution added at slow rate to form solution (neutral). The epoxide layer (reaction) is separated, dried with sodium sulfate and vacuum distilled.	NaOH and HCl, sodium carbonate and NaOH solution are reacted at approximately 150°F and 10 psi for 10 minutes; vacuum resin (reaction) is then vacuum distilled under heat and pressure to remove excess acid and water removed by heating, and clear resin poured from bath and cooled to solid.	Status of this type are prepared by reacting a phenolic-type novolac resin with epichlorohydrin under conditions somewhat similar to those used for conventional epoxy resins.					A polyetheric resin as butadiene in first polymerized and then reacted with peroxide acid to produce the specified polyetheric resin.	
6. Reaction type	Diglycidyl ether	Diglycidyl ether	Diglycidyl ether					Peroxide acid	
7. Form of reaction resin	Liquid	Solid	Solid					Solid	
8. General resin properties	Light yellow 100-400 parts @ 77°F Approx. 1.25 100-400 Most all organic solvents	Yellowish — 400-500 Ketones, alcohols, aromatic hydrocarbons Stable temperature to 150°F One year	Light yellow 100-400 parts @ 77°F Approx. 1.25 100-400 Ketones, alcohols, aromatic hydrocarbons Stable temperature to 150°F One year					Light yellow 100-400 parts @ 77°F Approx. 1.25 100-400 Ketones, alcohols and aromatic hydrocarbons Stable temperature to 150°F One year	



	Conventional Epoxy Resins ^a	Epoxy Novolac Resins ^b	Epoxythiol Polyesters ^c
10. Dielectric characteristics	Comprise 95% of all epoxy resins used; least expensive among all epoxies	Same	Contains reactive double bonds permitting use in production of vinyl-type materials and provides excellent glass characteristics. Tensile stresses below threshold (1,000).
11. Curing agents	See Table II-3 for conventional epoxy resin curing agents	Same	Curing agents for the epoxythiol polyesters are predominantly polythiols and include such as trimers, hexamethylenetriamine, bisoxazolones, guanidines. Epoxythiol resins are polymerized with polythiols, such as trimers. Typical systems: hexamethylenetriamine + 4-EPH; bisoxazolones + 4-EPH; guanidines + 4-EPH. Cure is effected at 100°F. Also used are polythiols and polyols (to be noted).
12. Physical use	Well known and proven laminating films when curing compounds, catalysts, fillers, tougheners, pigments and colorants. May be made flexible (compounds, tougheners, hard plasticizers, or special hardeners) and may be made self-extinguishing (halogen type).	Filled and used and backed coatings, varnishes	High-temperature structural and adhesive laminates (theraps, epoxy and chloro-phenolics); also composites, coatings, tougheners, adhesives, and high-temperature resins. Usually prepared to suit functionality.

TABLE II-2.3. CURING AGENTS FOR CONVENTIONAL TYPE EPOXY RESINS

Type of Resin	Typical Curing Agent Properties	Characteristics of Resin-C. A. System	Material	Example		
				PER for Curing Heat Deflection Temp.	RT Pot (hr) at Curing Temp.	Heat Deflec- tion Tempera- ture (after test seconds)
1. Primary aliphatic polyamines ^{a, b}	Low-viscosity liquids; disagreeable odor; irritating vapor; skin sensitizers.	Promote rapid cure at R. T. with short pot life and high exotherm; postcuring increases heat-deflection temperature; improves chemical resistance and electrical properties.	Diethylene triamine	12	20 min	177
			Triethylene tetramine	12	20 min	248
			Diethylamino-propylamine	8	RT (5 hr not cured)	210
			Dimethylamino-propylamine	4	Cure: 2 hr-250°F Set: 6 hr	248
2. Modified primary aliphatic polyamines	Liquids with viscosities similar to conventional resins; odor less noxious than No. 1; lower skin-sensitizing potential than No. 1.	Provide more convenient mixing ratios; faster curing, somewhat lower irritation potential; lower vapor pressure; tend to reduce physical & chemical properties.	Amine resin adduct	24	20 min	157
			Amine ethylene oxide adduct	20	15 min	194
			Cyanosilylation product	22.5	42 min	180
			Amine phenol (proprietary mixture)	18.5	11 min	233
3. Cyclic aliphatic amines	Low-viscosity liquids; vary from mild to strong vapors.	Long pot life; low exotherm possible; postcure usually required.	Piperidine	10	Thick gel: 2-6 hr Set: 22-48 hr	183
			N-aminomethyl piperazine	18	18 min	233
4. Aromatic amines	Solids (some proprietary aromatic amines are liquids); irritating vapor.	Higher heat-deflection temperatures than aliphatic amines; can be used for B-staging.	Metaphenylene diamine ^a	21	0-18 hr	227
			Diamino diphenyl sulfone ^a	20	Cure: 1 hr-300°F	247
			Dicyandiamide (with solid resins)	4	Cure: 1/2 hr-345°F	—

5. Tertiary amines	Low-viscosity liquids; mild odor; low skin-sensitizing potential.	Long pot lives; can be used as accelerators for polyamides and anhydride cures.	Dimethylamino ethanol	4	Thick gel: 0-6 hr Set: 0-15 hr	234
			Benzyldimethylamine	9	Thick gel: 6 hr Set: 0-15 hr	185
6. Latent curing agents	Liquids and solids.	Long pot lives; cure activated by heat.	Boron trifluoride-monoethylamine complex	2-4	7 to 30 days	—
			Triethanolamine borate	—	Cure: 1 hr-250°F	233
7. Polyamides ^{a, b}	Medium to high-viscosity liquids; mild odor; low skin-sensitizing potential.	Impart flexibility to resins when cured.	Reaction product of ethylene diamine and the dimer of isocyanic acid	64	150 min	220
8. Acid anhydrides ^{a, b}	Solids or liquids; corrosive and some are lachrymatory, but have low skin-sensitizing potential.	High heat-deflection temperatures; high-temperature resistance; superior electrical properties; require elevated temperature cures.	Phthalic anhyd.	40-60	Cure: 3 hr-300°F	150
			Maleic anhyd.	—	—	—
			Dodecylsuccinic anhyd.	120-150	Cure: 6 hr-300°F	158
			Chlorosulfonic anhyd.	100-120	Cure: 3 hr-320°F	256
			Pyromellitic dianhydride ^a and	FMDA- (15-21) to MA-(19-27)	Cure: 24 hr-320°F	275-300
			Maleic anhyd. mixtures	—	—	—
			Hexahydrophthalic anhyd.	60	Cure: 2.5 hr-225°F	424

^a Room temperature pot lives given for 100-gm epoxy resin plus hardener; equivalent weights of resin = 100.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

ThreeBond TECHNICAL NEWS

Three Bond Technical News
Issued October 1, 1987

19

One-Part Epoxy Resin

Introduction

In addition to two-part epoxy resin, one-part epoxy resin has a wide range of applications. However, it seems that the product has not readily been and accurately understood by many people.

According to the survey conducted internally, one-part epoxy resin ranked high in both the "salable" and "difficult to sell" groups, giving a rather puzzling result. After all, though this is my own interpretation, sellers and buyers who have a

certain degree of knowledge and understanding of one-part epoxy resins can select and use them, while those who consider it difficult to sell the resins may not understand the versatility and wide range of applications of epoxy resin.

This issue of the newsletter describes one-part epoxy resin, which has various properties and a wide range of uses, in order to increase understanding of the resin.

Contents

Introduction	1
1. Summary	2
2. Demand for epoxy resin in various fields	2
3. What is epoxy resin?	2
4. Compounding ingredients of epoxy-resin and roles thereof	4
4-1. Major types of epoxy resin	5
4-2. Various curing agents	5
< Dicyandiamide and derivatives thereof >	5
4-3. Elasticity and shock-resistant agents	6
4-4. Heat-resistant agents	7
4-5. Fillers	7
4-6. Diluents	8
4-7. Thixotropic agents	8
5. Major properties and uses of one-part epoxy resin	8
Conclusion	10

1. Summary

One-part epoxy resin has some commonalities with two-part epoxy resin. For example, they use the same epoxy resin, which is the fundamental ingredient thereof, and have employed very similar methods of improvement and development. In addition, the one-part technique is primarily dependent on the curing agents used. Therefore, the compounding techniques described in the present report should be understood as regarding general epoxy-resin compounds. Epoxy resin is characterized by the high degree of flexibility in its compounds due to its stability. Various compound techniques have been suggested and discussed for exploiting the flexibility and other good properties of the basic types of epoxy resin. This report describes the basic properties of the epoxy resin and the ingredients of the compounds and the roles thereof, and introduces the properties and uses of one-part epoxy resin.

2. Demand for epoxy resin in various fields

As shown in Table 1, there is demand for epoxy resin in a wide range of fields, including paints and electrical components. As a trend over the past

decade, the focus of the demand has shifted from general paints to automobile paints, and then to electrical components. In particular over the past few years, there has been increasing demand for the resin as an encapsulating material of IC and LSI for electrical machinery such as FA and OA appliances.

3. What is epoxy resin?

The term "epoxy resin" is a generic name for compounds that have two or more oxirane rings (epoxy groups) in one molecule, and are cured three-dimensionally by a suitable curing agent. However, in most cases, the term refers to bisphenol-A diglycidyl ether (DGEBA), which is formed by the reaction between bisphenol A and epichlorohydrin, which currently commands a 75% share of the epoxy-resin market. Of the products of Three Bond, 50% to 60% of one-part epoxy resin and more than 90% of two-part epoxy resin are based on DGEBA or compounds containing DGEBA. Therefore, DGEBA is synonym for epoxy resin.

The following section describes the structure and performance of epoxy resin, using DGEBA as a representative example.

Table 1. Delivery quantity of epoxy resin organized by use
(year on year (%)) 87-01-26

Uses \ Year		54		55		56		57		58		59	
Paints	Cans	5,643		4,973	88	6,378	128	5,836	92	7,234	124	8,258	114
	Automobiles			6,458	157	7,808	121	9,595	123	10,514	110	11,534	110
	Ships	3,739		4,929	132	7,533	153	7,496	100	6,888	92	7,572	110
	General purposes	11,191		10,578	95	10,153	96	9,713	96	10,974	113	13,412	122
	Total	24,676		26,938	109	31,872	118	32,640	102	35,610	109	40,776	115
Electrical components	Laminates	7,118		7,364	103	9,982	136	10,362	104	14,142	136	20,864	148
	Casting	5,282		5,367	102	4,574	85	3,658	80	4,079	112	5,266	129
	Others	2,231		2,260	101	3,413	151	3,652	107	5,483	150	11,122	203
	Total	14,631		14,991	102	17,969	120	17,672	98	23,704	134	37,252	157
Civil construction		6,901		6,558	95	7,411	113	8,002	108	9,446	118	9,469	100
Adhesives		3,582		3,659	102	3,832	105	3,609	94	3,731	103	3,882	104
Others		6,404		6,407	100	5,296	83	4,778	90	6,238	131	7,646	123
Domestic demand total		56,194		58,553	104	66,380	113	66,701	100	78,729	118	99,025	126
Export		915		902	99	568	63	866	152	1,330	154	1,729	130
Grand total		57,109		59,455	104	66,948	113	67,567	101	80,059	118	100,754	126

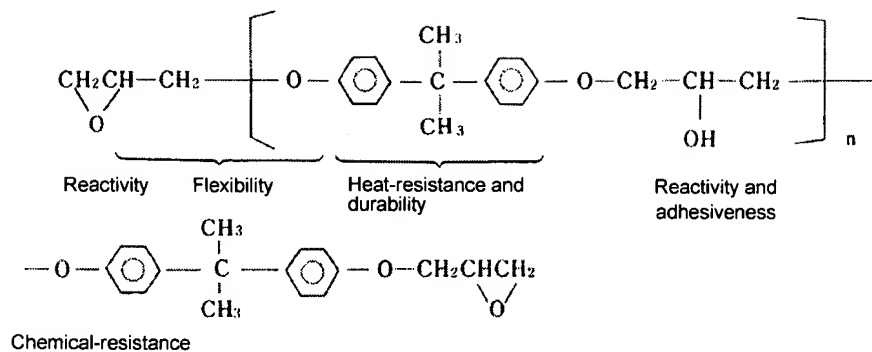


Fig. 1. Structure and properties of epoxy resin

The excellent properties of epoxy resin, such as durability and adhesiveness, depend largely on its structure. Fig. 1 shows the relationship schematically.

- 1) The epoxy groups at both terminals of the molecule and the hydroxyl groups at the midpoint of the molecule are highly reactive, allowing room-temperature and high-temperature curing using suitable curing agents, and a wide range of modifications. In addition, the resin is cured by ring-opening polymerization, and as a result has a smaller
- degree of cure shrinkage than other thermosetting resins.
- 2) The ether linkages included in the main chain improve the chemical-resistance and elasticity.
- 3) The benzene rings in bisphenol A provide chemical-resistance, adhesiveness, durability, heat-resistance and excellent electrical properties.
- 4) The coexistence of hydrophilic groups with hydrophobic groups in the molecule significantly increases the adhesion to various adherends.

60		61•Breakdown								61•Total	
		1 ~ 3		4 ~ 6		7 ~ 9		10~12			
8,327	101	2,051	93	2,697	116	2,397	127	2,279	119	9,424	113
12,473	108	2,988	101	3,095	91	3,013	100	3,103	100	12,199	98
7,437	98	1,411	73	1,584	78	1,515	85	1,514	88	6,024	81
13,122	98	3,294	104	4,100	121	3,561	113	3,497	103	14,452	110
41,359	101	9,744	95	11,476	103	10,486	107	10,393	103	42,099	102
18,652	89	4,436	100	5,973	133	5,453	110	5,791	121	21,653	116
5,565	106	1,663	121	1,873	136	1,898	139	2,142	148	7,576	136
10,849	98	3,215	102	4,044	144	4,130	193	3,689	135	15,078	139
35,066	94	9,314	104	11,890	137	11,481	136	11,622	130	44,307	126
9,349	99	2,210	92	2,017	96	2,347	96	2,273	95	8,847	95
4,059	105	1,019	105	1,358	138	1,316	133	1,478	133	5,171	127
7,768	102	2,007	95	1,751	97	1,867	101	1,925	97	7,550	97
97,601	99	24,294	98	28,492	115	27,497	117	27,691	113	107,974	111
1,423	82	583	139	521	180	420	111	437	130	1,961	138
99,024	98	24,877	99	29,013	116	27,917	117	28,128	113	109,935	111

As described above, many properties are ascribable to the structure, but such properties are largely dependent on the curing agents that cause the curing reaction, resulting in wide selectivity of the epoxy resin.

4. Compounding ingredients of epoxy-resin and roles thereof

As shown in Table 2, regardless of whether it is one-part or two-part, epoxy resin is rarely used alone as an epoxy-resin material, but rather is used in the form of compounds containing various

modifiers and diluents in order to impart the resin's desirable properties, such as strength, flowability, and heat-resistance.

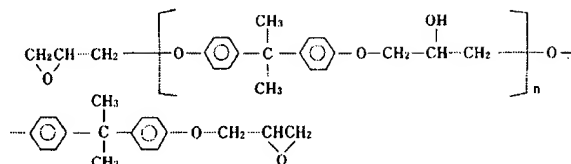
In addition to the agents described below, various agents can be mixed with epoxy resin. In such cases, epoxy resin causes remarkably less gelation and reaction inhibition than other reactive resins, which gives a significant advantage to the resin in the creation of compounds and allows anyone to make such compounds.

Table 2. Compounding ingredients of epoxy-resin and roles thereof

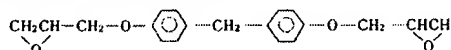
Constituents	Ingredients	Roles
Resin content	Epoxy resin	The bisphenol-A type is common. However, there are many other types of epoxy resin having different properties.
	Curing agents	Curing agents react with epoxy groups to form a three-dimensional network structure by crosslinking.
Modifying ingredients	Elasticity agents	Elasticity agents elasticate compounds to improve their peeling strength and extensibility, e.g., elasticizers and epoxy modifying resins.
	Shock-resistant agents	Shock-resistant agents eliminate brittleness from epoxy resin to prevent cracks and decrease distortion.
	Fillers	Fillers increase the weight in order to decrease costs and improving various types of mechanical strength, e.g., calcium carbonate and talc.
	Heat-resistant agents	Heat-resistant agents increase the heat-resistance and heat-deformation temperature through the use of multi-sensual types of epoxy resins such as novolac epoxy resin.
	Diluents	Diluents reduce viscosity and improve flowability and permeability. Reactive diluents having epoxy groups and nonreactive diluents having no epoxy group are available.
	Thixotropic agents	Thixotropic agents impart thixotropy to compounds in order to control flowability and increase viscosity.
	Other agents	Pigments, coupling agents, defoaming agents, leveling agents, etc.

4-1. Major types of epoxy resin

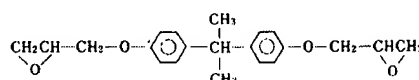
Bisphenol-A type (DGEBA); Commonly used



Bisphenol-F type; Characterized by having low viscosity



Bisphenol-A D type; Having intermediate characteristics between those of the DGEBA and bisphenol-F types



Most epoxy resins are composed on the basis of the above three types of resin. There are many other types of epoxy resins; however, most are not adaptable to a wide variety of applications, and rather are intended for special purposes such as modifications and improvements to heat-resistance and elasticity.

4-2. Various curing agents

Like epoxy resin, there are various types of curing agents for epoxy resin. In fact, there are so many types that they cannot be covered in this report; therefore, only the latent curing agent for one-part epoxy resin is described in this section.

The types of latent curing agents are classified as shown in Table 3. Including our products, those that are commercially available are primarily of the thermosetting type. Most thermosetting curing agents are of the dissolution-reactive type.

Table 3. Classification of latent curing agents

Activation means	Phenomena	Curing agents
Heat activation	Ionic reaction	Lewis-acid complexes (BF ₃ -ME-A, etc.)
	Dissolution	Dicyandiamide Modified imidazole, organic acids Hydrazides, DCMU
	Decomposition	Amine-imide compounds
	Elution	Molecular sieves
Light (UV)	Microcapsules	
	Decomposition	Aromatic diazonium salts, diallyl iodonium salts, triaryl sulfonium salts
Moisture	Decomposition	Ketoimine
	Elution	Molecular sieves
Pressure	Microcapsules	

Using dicyandiamide as a representative example, the following section describes the characteristics

and properties of thermal-dissolution reactive curing agents.

<Dicyandiamide and derivatives thereof>

Dicyandiamides are crystals with a high melting point of 207°C to 210°C. When dispersed in epoxy resin in the form of fine powder, they will have a pot life of 6 to 12 months, and will remain stable for a greater length of time than imidazole. Four to ten parts of them are added to DGEBA.

Dicyandiamides require heating at 160°C to 180°C for one hour to several hours for curing, and generate a large quantity of heat upon curing. They tend to sediment due to their high specific gravity, and thus are not suitable for casting. They are used for coating, adhesion, and lamination.

In many cases, to decrease the curing temperature, which is a weakness of dicyandiamides, an accelerating agent is added, as shown in the following example of compound, in order to accelerate curing at a lower temperature. New accelerating agents have actively been developed.

<Example of compound>

DGEBA 100 * H₂N—C—NH—CN
DICY (dicyandiamide*) 8 ||
Dimethyl urea 3 NH

<Properties of the compound>

Curing conditions 120 °C × 30 minutes
Shearing strength 150 kg/cm²
Glass transition point 125 °C

The compound has found a wide range of applications: as an adhesive in electric and electronic applications, as an encapsulating material for terminals due to the fact that it does not cause metal corrosion, as a structural adhesive due to its

strong adhesiveness, and for pre-preg and powder coating due to its low cost.

4-3. Elasticity and shock-resistant agents

Despite its high strength, (cured) epoxy resin has the problem of brittleness due to its poor elasticity. One-part epoxy resin, when it has not been particularly elasticated, has shearing adhesive strength of 150 to 200 kgf/cm², which is relatively high for an adhesive; however, it has peeling adhesive strength of 0.5 to 1 kgf/25 mm width in a T-peel test, which is equivalent to that of instant adhesives. This is due to the fact that the cured resin is relatively low in extensibility. If this insufficiency is redressed by an elasticity agent, the resin may have shearing adhesive strength of 250 kgf/cm² or higher, and peeling adhesive force of 20 kgf/25 mm width in a T-peel test.

The elasticated agents are described below.

The purposes of adding elasticated agents include the following: 1) improvements in mechanical strength, 2) prevention of cracks due to thermal distortion, and reduction of distortion, and 3) improvements in adhesiveness, particularly

improvements in peel strength by imparting elasticity to disperse stresses.

The method of compounding elasticated agent is as follows: an elastic structure is introduced to the main chain polymer, side chain or terminal of a bisphenol type resin (see Fig. 2). However, the introduction of polymers having a rubber structure or a straight chain inevitably causes a significant increase in the viscosity of the material and deterioration of the properties of the material, such as heat-resistance, due to the decrease in the crosslinking density.

To avoid such deteriorations in properties, a special elasticated agent, carboxyl-terminal butadiene-acrylonitrile copolymer liquid rubber (CTBN), may be added. CTBN has mutual solubility with epoxy resin, but does not have it with cured epoxy resin and therein forms a dispersed rubber particle phase, and serves as a cushioning material to prevent cracks (see Fig. 3). This elasticated agent is said to provide elasticity without deteriorations in properties, due to the fact that it does not remain in the epoxy-resin layer.

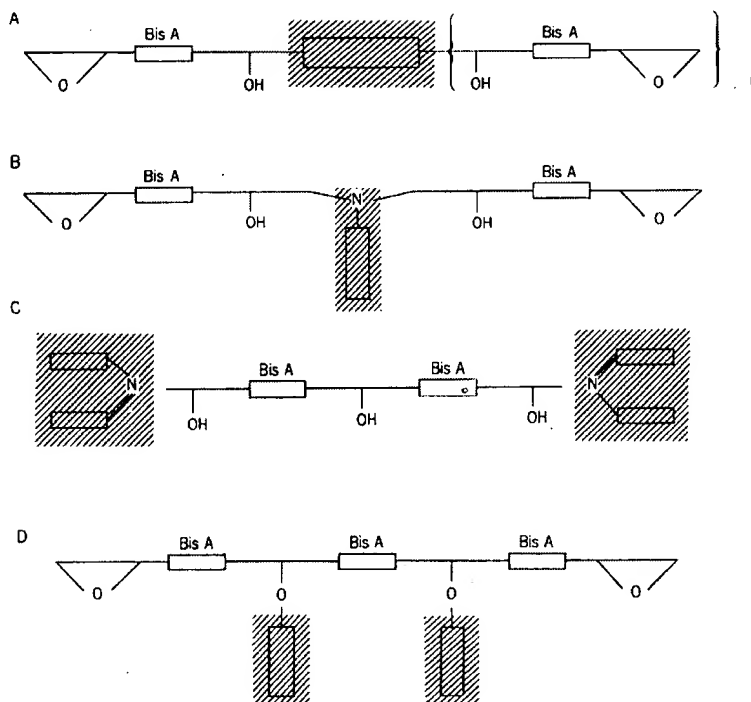


Fig. 2. Schematic structure of modified resins

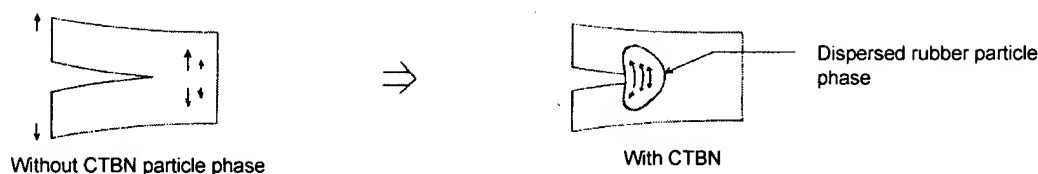


Fig. 3. Effect of CTBN

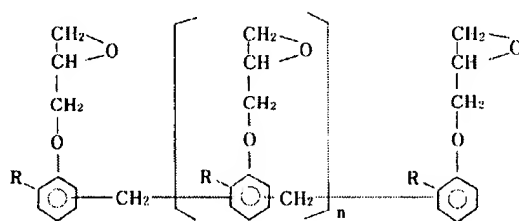
4-4. Heat-resistance improvers

The heat-resistance of compounds depends primarily on the epoxy resin contained therein. In one-part epoxy resin, the usable curing agents are limited, and thus the heat-resistance depends primarily on the type of selected epoxy resin.

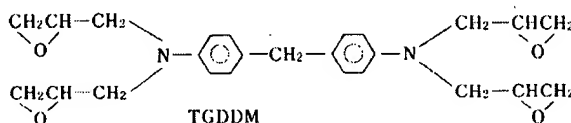
It can be generally concluded that improvements in crosslinking density contribute to improvements in heat-resistance, and thus resins with a short distance between epoxy groups, or multifunctional types of epoxy resin are commonly used.

Representative examples are given below.

Novolac epoxy resin



Glycidyl amine resin



Glycidyl ether resin

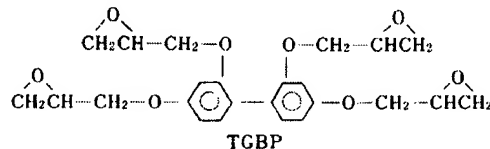


Fig. 4. Representative heat-resistance agents

4-5. Fillers

Fillers tend to be regarded merely as bulking agents, but their roles cannot be neglected due to the fact that increasingly rigorous properties are required of epoxy resin. It is therefore necessary to select and add appropriate fillers.

The effects of fillers include the following:

- 1) Improvements in mechanical strength
- 2) Reduction in thermal distortion and dimensional change
- 3) Improvements in electrical properties, particularly insulating and dielectric properties
- 4) Cost reduction due to the increase in weight
- 5) Improvements in fire retardancy

6) Improvements in heat conductivity

4-6. Diluents

As previously mentioned, when various materials are added to epoxy resin in order to improve its properties, the viscosity of the composition correspondingly increases. Bisphenol-A-type epoxy resin itself does not have low viscosity, and thus it inevitably requires adjustment (reduction) of its viscosity. For this purpose, diluents are used.

The influence of diluents on performance must be minimized, and thus the preferably used fillers are those that can have a significant effect with as small amounts as possible. One-part epoxy resin requires diluents having a low vapor pressure, as it undergoes a heating process.

Diluents fall into two types: reactive ones having epoxy groups and unreactive ones having no epoxy group. Most one-part epoxy resins are used reactive diluents, as unreactive diluents serve as a plasticizer in the cured resin. Fig. 5 shows the major diluents. Their handling requires caution, as they have a low molecular weight and readily permeate through the skin to cause irritation.

4-7. Thixotropic agents

Thixotropy is a property of liquids containing flocculating components. Flocculating components are destroyed by repeated stirring and the liquids show flowability; however, once stirring is stopped, the components reflocculate and the liquids return to the nonflowable state.

This property is required in applications in which sagging causes a problem, such as the thick coating of paints and the adhesive sealing of gaps. Commonly used effective thixotropic agents include silica fine powder (Aerosil), and colloidal hydrated aluminum silicate/organic complex (Orben).

However, the effect varies among thixotropic agents. Some exert their effect in heating, and others disappear in heating, become ineffective when cured, or deteriorate over time. Their selection is difficult even for experts.

5. Major functions and uses of one-part epoxy resins

Table 4 lists the major properties and uses of one-part epoxy resin, and Photograph 1 shows examples of the usage of one-part epoxy resin.

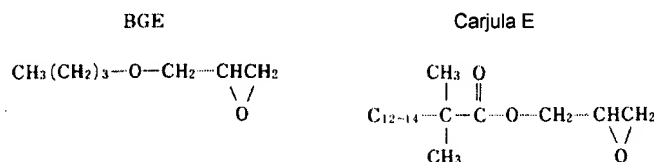
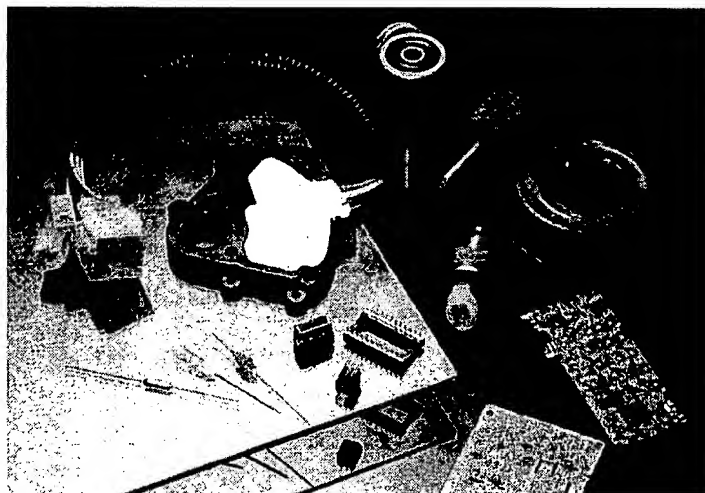


Fig. 5 Representative reactive diluents

Table 4. Major properties and uses of one-part epoxy resin

Properties	Uses	Characteristics	Product name ("TB" is an abbreviation for Three Bond.)
Heat-resistance	(1) Impregnating fixation of armature coils	Moderate impregnation properties and strength with heating at 160 °C or higher Resistance to continuous heating at 220 °C	TB2068K, TB2068H TB2064C
	(2) Heat-resistant adhesion	Glass transition temperature of 170 °C, strength with heating 200 °C, 50 kgf/cm ² , peeling strength of 14 kgf/25 mm width	TB2064C
	(3) Adhesion of motor magnets	Moderate flowability, strength with heating at 150°C or higher	TB2068M
Dimensional stability	(1) Encapsulation of heads and electrical components	Low coefficient of thermal expansion, high moisture-resistance, high purity, resistance to P.C.T. (pressure cooker test)	TB2071B
Thixotropy	(1) Antisagging, temporal adhesion of chips, fixation of coil terminals	High thixotropy, screen printability Fast curing at 150 °C, curing in one to two minutes	TB2065, TB2065M
	(2) Terminal seal for prevention of penetration	Moderate flowability, curing at a low temperature of 80 °C to 100 °C	TB2062B, TB2062D
	(3) Joint sealants	High thixotropy, high viscosity	TB2065, TB2062K
Fast curing	(1) Adhesion of syringe needles	Moderate permeability, white cured substance, curing at 150 °C in one to three minutes	TB2062D, TB2065L
	(2) Coating of stepping motors	Curing at 150 °C in one to three minutes, machinability	TB2065, TB2065C
Machinability	(1) Joint sealants for bus bodies	High shock adhesive force, slump property, and machinability	TB2063C
Impregnation	(1) Low-viscosity impregnating adhesion, impregnation of cut cores	Low viscosity, long shelf life	TB2076, TB2076C
	(2) Potting agent for small coils	Low viscosity, low shrinkage ratio	TB2071C
Elasticity	(1) Thermal shock, adhesion of motor magnets	Absorption of the thermal distortion of magnets/yokes, prevention of cracks in vibration-absorbing magnets	TB2064, TB2064B
	(2) Terminal seal for halogen-lamp	Thermal shock, conformity to terminal bending, adhesion to engineering plastics	TB2064
	(3) Adhesion of headlights (iron/glass)	Rubber elasticity	TB2067E, TB2067F TB2067D
Structural adhesion	(1) Adhesion of automobile hemming	High adhesive strength, peeling adhesive force	TB2068G
	(2) Adhesion of joints in chainsaw fuel tanks	High adhesive strength, peeling adhesive force	TB2063, TB2063D
Filling adhesion	(1) Potting of inhibitor switches	Moderate flowability, heat-resistance, weather-resistance	TB2068M, TB2068P TB2068I, TB2063J
	(2) Adhesion sealing of plastic cases	Moderate permeability, soldering heat-resistance	TB2062C, TB2062J
	(3) Encapsulation of printer heads	Moisture-resistance, flowability, low-temperature fast-curing property	TB2065E, TB2065F



Photograph 1 Examples of the usage of one-part epoxy resin

Conclusion

Three Bond has been selling one-part epoxy resin for more than ten years. In that time, we have developed various grades of products, such as a simple compounds composed of a bisphenol-A-type epoxy resin, dicyandiamide, and a filler, and those containing a low-temperature active curing agent for curing at 80 °C, as well as those comprising a heat-resistant resin to achieve high heat-resistance and those allowing a peeling adhesive force of 10 kg/25 mm width or more through rubber modification. The performance of these products has been proven.

Thanks to an increase in the demand for one-part epoxy resin and the development of various functional materials as a result of the efforts of material manufacturers, we have successfully developed proven products. We will continue to work to expand the possibilities of one-part epoxy resins.

Yukimasa Osumi
Adhesive laboratory
R&D Laboratory

ThreeBond
TECHNICAL NEWS

THREE BOND CO., LTD.

1456 Hazama-cho, Hachioji-shi, Tokyo 193-8533, Japan
Tel: 81-426-61-1333



Intermediates & Polymer

[Overview](#) [Product Info](#) [Location Info](#) [Contact](#) [Home](#)

Specialty Products

[Specialty Products](#)

Terate® Polyols

- [Aromatic Polyols From the Complete Polyester Resource](#)
- [A Leader in the Industry](#)
- [Our Growth](#)
- [Product Advantages](#)
- [Standard Product Information](#)
- [Guidelines for Storage and Handling](#)
- [Availability and Reliability](#)
- [Customer Service, Sales, and Technical Information](#)

Aromatic Polyols From the Complete Polyester Resource



KoSa offers a diverse line of Terate® aromatic polyester polyols for use in polyurethanes. Our polyols are available in a wide variety of equivalent weights and properties to allow for formulation flexibility. Processes using Terate polyols achieve the rigorous physical and flammability properties required in many rigid polyurethane (PUR) and polyisocyanurate (PIR) foams. The high aromaticity of Terate polyols, along with their low cost, makes them extremely desirable for many applications.

In flammability tests, PIR and PUR foams containing Terate polyols result in excellent char formation with minimal shrinkage and high weight retention.* In many formulations, the unique aromatic backbone of Terate polyols reduces or eliminates the need for expensive flame retardants.

* As demonstrated in ASTM E-84 and Factory Mutual calorimeter testing with HCFC 141b, pentane, and partially water-blown foams.

[back to top](#)

A Leader in the Industry

New product development, experienced technical service and computerized process control make KoSa's Terate polyols an industry leader. Market demands, such as blowing agent replacement and increased polyester polyol ratios, create challenges for foam formulators. KoSa's Terate professionals work proactively with customers and co-suppliers to develop optimal Terate-based PUR and PIR formulations.

As the world's largest producer of dimethyl terephthalate (DMT) - the raw material source for Terate Polyols - we can ensure that our customers receive an uninterrupted supply of consistent, high-quality products.

[back to top](#)

Our Growth



Our Terate polyols were first produced in 1974 by Hercules at its Wilmington, NC, USA, site. Since 1989 when the current Terate team was formed, production has increased eight-fold and continues to increase at our newest production facility in Vlissingen, Netherlands.

Although our name has changed over the years - from Hercules to Cape Industries to Hoechst Celanese, and now to KoSa - our commitment to polyester and new applications for Terate polyols has remained constant. With continued enhancements of our products, KoSa provides the best polyester polyols for many applications in the urethane industry.

[back to top](#)

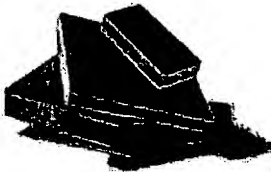
Product Advantages

KoSa Terate polyols are ultimately designed to give our customers greater flexibility and control with their products. Additionally, our experience and capabilities provide customers with:

- Industry-leading technical service in formulation and production
- Reliable supply of internal raw material available
- Computerized quality process control
- Excellent flame-resistance results
- Multi-property product line
- Consistent quality products
- Blowing agent compatibility
- Cost advantage over polyethers
- High aromatic content
- Good flow properties
- Uniform reactivity

[back to top](#)

Standard Product Information



Terate polyols are available in the following basic series featuring a variety of options in color, viscosity, acidity, processability, hydroxyl value and functionality. This list includes typical property ranges for each series. Please refer to data sheets available from your KoSa representative for actual product specifications and applications.

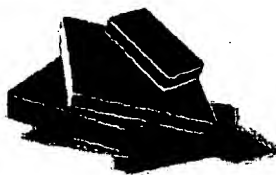
Value Range						
Product Series	Hydroxyl Value (mgKOH/g)	Viscosity (cps@25°C)	Functionality	Acidity (mgKOH/g)	Average Equivalent Weight	Specific Gravity (g/ml)
Terate 2000	280 - 335	3,000 - 22,000	2.3	0.5 - 4.0	181	1.2
The original Terate polyol with high functionality use in bunstock, panel, pour-in-place, spray and foundry systems. Available in lower acid numbers.						
Terate 2500	225 - 275	2,700 - 7,700	2.0	0.4 - 2.0	238	1.2
A polyol series with excellent flammability in polyisocyanurate foams with minimal shrinkage and high weight retention. In many formulations, the unique aromatic backbone reduces or eliminates expensive flame retardants. Used in laminate, panel, pour-in-place and spray systems.						
Terate 3000*	230 - 255	2750 - 7,500	2.0	0.6 - 1.2	230	1.2
A series of polyols developed for hydrocarbon blown foam applications with improved characteristics over the 2500 series.						
Terate 4000*	295 - 350	1,500 - 6,000	2.0 - 2.2	0.2 - 1.5	175	1.2
An amber polyol series used in appliance systems and for other low viscosity requirements. Similar to our 2000 series, but with reduced viscosity.						
Phenrez®*	50 - 100	700 - 10,000	-	2.0 - 10	-	1.13
A dark, high-polar, liquid aromatic polyester resin used in foundries producing furan no-bake (FNB) resin systems.						

SEE MATERIAL SAFETY DATA SHEET FOR SAFETY INFORMATION. Because we cannot anticipate or control the many different conditions under which this information and our products may be used, we do not guarantee the applicability or the accuracy of this information or the suitability of our products in any given situation. Users of our products should conduct their own tests to determine the suitability of each such product for their particular purposes. The products discussed are sold without warranty, either expressed or implied, and the buyer assumes all responsibility for loss or damage arising from the handling and use of our products. Additionally, statements concerning the possible use of our products are not intended as recommendations to use our products in the infringement of any patent.

*Please check with a KoSa representative about availability in your area.

[back to top](#)

Guidelines for Storage and Handling



Terate polyols can be stored and handled in tanks made of carbon steel, stainless steel, fiberglass or other conventional construction materials. Storage temperatures should be kept below 60°C (140°F) to maintain product integrity. Storage vessels and process tanks also should be protected with dry air [minimum 4.4°C (-40°F bulb)] or nitrogen to prevent uptake of atmospheric moisture. Please see the MSDS for specific details on handling individual products.

[back to top](#)

Availability and Reliability

Terate polyols are shipped worldwide in lined, closed-head drums, tank trucks, and tank cars from KoSa's US and European facilities. Samples are available upon request. Our Terate polyol team will be glad to arrange a delivery system to best meet your needs.

Terate® and Phenrez® are registered trademarks of KoSa.

[back to top](#)

Customer Service, Sales, and Technical Information

Inside the United States, dial toll-free 1-800-562-0172

Outside the United States, dial:

North America, South America and Asia

Customer Service 1-910-341-5947

Fax 1-910-341-5951

Europe, Africa and Middle East

Customer Service 49(0)-69-305-14789

Fax 49(0)-69-305-16315

[back to top](#)

©1999 KoSa. All rights reserved.

[Terms and Conditions](#)

Site managed by [Excelorant](#).



Up

About Polyols

Synair Corporation
Post Office Box 5269
2003 Amnicola Highway
Chattanooga, TN 37406
USA

(423) 687-0400 main
(423) 687-0443 fax

Polyurethanes are based the exothermic reaction of polyisocyanates and polyol molecules. Many different kinds of polyurethane materials are produced from a few types of isocyanates and a range of polyols with different functionality and molecular weights. Some of the diversity of functionality depends on whether the polyols are based on polyether or polyesters. Condensation based polyols are used primarily in the construction and building industries for efficient insulation in roofs, wall cavities, and flooring. Polyether polyols are used in a wide range of rigid and flexible polyurethane applications, including energy saving refrigeration insulation, industrial sealants, cushion foam, and construction and building materials.

Polyether polyols contain the repeating ether linkage $-R-O-R-$ and have two or more hydroxyl groups as terminal functional groups. They are manufactured commercially by the catalyzed addition of epoxies (cyclic ethers) to an initiator. The most important of the cyclic ethers by far are propylene oxide and ethylene oxide, with smaller quantities of butylenes oxide also being consumed. These oxides react with active hydrogen-containing compounds (called initiators), such as water, glycols, polyols and amines; thus, a wide variety of compositions of varying structures, chain lengths and molecular weights is theoretically possible. By selecting the proper oxide (or oxides), initiator, and reaction conditions and catalysts, it is possible to synthesize a series of polyether polyols that range from low-molecular-weight polyglycols to high-molecular-weight resins. Most polyether polyols are produced for polyurethane applications; however, other end uses range from synthetic lubricants and functional fluids to surface-active agents.

Since these polymers contain repeating alkylene oxide units, they are often referred to as polyalkylene glycols or polyglycols. The terms *polyglycol* and *polyether polyol* are used interchangeably; however, the term *polyalkylene glycol* is used when these types of products are used in nonpolyurethane applications. The physical properties of the polyols are influenced primarily by the functionality of the initiator molecules and by the type and quantity of alkylene oxide and hydroxyl groups present in the polyol. In general, the functionality of the polyether is carried over from the functionality of the initiator used.

Two types of urethane polyols are prepared from propylene oxide. The first type results from the reaction of propylene oxide with compounds having an active hydrogen (usually donated by a hydroxyl or amine group); these polymers are typically atactic. Polymers of the second type are essentially those of propylene oxide itself and are commonly called polypropylene oxide or polypropylene glycol; they are in most cases isotactic. Mixtures of atactic and isotactic polymers may also occur.

The following table lists most of the major commercially available polyether polyol types used in urethane manufacture, plus the initiators and cyclic ethers (oxides) used in their preparation:

Selected Commercial Polyether Polyols and Reactants

Product	Initiator	Cyclic Ether
Difunctional <ul style="list-style-type: none"> ➤ Polypropylene Glycol (PPG) ➤ Polyethylene Glycol (PEG) ➤ Polyoxypropylene-Polyoxy-ethylene Block Copolymer ➤ Polytetramethylene Ether Glycol (PTMEG) ➤ Aromatic Diol ➤ Amine Adducts 	<ul style="list-style-type: none"> ➤ Water or propylene glycol ➤ Water or ethylene glycol ➤ Water, propylene glycol or glycerin * ➤ Water ➤ Bisphenol A ➤ Primary monoamines ** 	<ul style="list-style-type: none"> ➤ Propylene oxide ➤ Ethylene oxide ➤ Propylene oxide and ethylene oxide ➤ Tetrahydrofuran ➤ Propylene oxide or ethylene oxide ➤ Propylene oxide or ethylene oxide
Trifunctional <ul style="list-style-type: none"> ➤ Glycerin Adduct ➤ Trimethylolpropane Adduct ➤ Trimethylolethane Adduct 	<ul style="list-style-type: none"> ➤ Glycerin ➤ Trimethylolpropane ➤ Trimethylolethane 	<ul style="list-style-type: none"> ➤ Propylene oxide ➤ Propylene oxide ➤ Propylene oxide
Tetrafunctional <ul style="list-style-type: none"> ➤ Pentaerythritol Adduct ➤ Ethylenediamine Adduct ➤ Phenolic Resin Adduct ➤ Methyl Glucoside Adduct 	<ul style="list-style-type: none"> ➤ Pentaerythritol ➤ Ethylenediamine ➤ Phenolic resin ➤ Methyl Glucoside 	<ul style="list-style-type: none"> ➤ Propylene oxide ➤ Propylene oxide ➤ Propylene oxide ➤ Propylene oxide
Pentafunctional <ul style="list-style-type: none"> ➤ Diethylenetriamine Adduct 	<ul style="list-style-type: none"> ➤ Diethylenetriamine 	<ul style="list-style-type: none"> ➤ Propylene oxide
Hexafunctional <ul style="list-style-type: none"> ➤ Sorbitol Adducts 	<ul style="list-style-type: none"> ➤ Sorbitol 	<ul style="list-style-type: none"> ➤ Propylene oxide or ethylene oxide
Octafunctional <ul style="list-style-type: none"> ➤ Sucrose Adducts 	<ul style="list-style-type: none"> ➤ Sucrose 	<ul style="list-style-type: none"> ➤ Propylene oxide

* Other compounds, including trimethylolpropane, trimethylolethane, pentaerythritol, ethylenediamine, sorbitol and sucrose, can also be used as initiators for block copolymers based on propylene oxide and ethylene oxide.

** Primary monoamines include aniline, cyclohexylamine and others. The compositions made from these amines and oxides are principally surface-active agents.

During the late 1980s, the polyurethane industry was faced with a major change in manufacturing practice to reduce foam blowing using chlorofluorocarbons (CFCs). The once widely used CFC-11 (CCl_3F) and, to a lesser extent, CFC-12 (CCl_2F_2), have been replaced with other blowing agents such as hydrochlorofluorocarbons (HCFCs) or other nonfluorocarbon-based blowing agents that have lower ozone depletion potentials. For some time, scientific data have shown that these "hard" fluorocarbons (they do not decompose) are the cause of an increasing depletion of the ozone layer above the earth's atmosphere.

The industry is working with two HCFCs: Cl_2FCH_3 , called HCFC-141b, and CHCl_2CF_3 , called HCFC-123. These materials decompose, permitting the production of polyurethane foams with acceptable performance characteristics, but they are more expensive than the hard fluorocarbons they are designed to replace. Commercial quantities of some of the new HCFCs have been available since 1992.

The industry has responded with the development of new manufacturing methods, machinery and auxiliary blowing agents to replace conventional fluorocarbon blowing agents. Flexible foam is produced using a water-blown technology—where the foam is blown by carbon dioxide gas generated when

water in the formulation reacts with toluene diisocyanate. Methylene chloride, acetone or hydrocarbons are sometimes used to replace some of the fluorocarbon. Rigid foams now use formulations with HCFCs replacing CFC-11.

MANUFACTURING PROCESSES

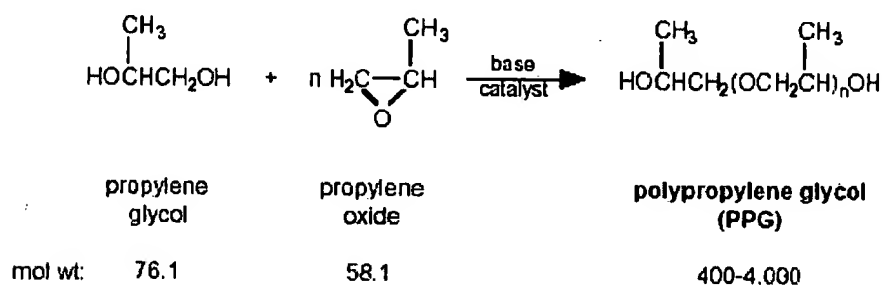
POLYOLS BASED ON PROPYLENE OXIDE

Polyether polyols based on propylene oxide (PO) are produced by the base-catalyzed reaction of propylene oxide with an initiator compound having active hydrogens (e.g., hydroxyl or amine groups). When small quantities of ethylene or other alkylene oxides are also present, block copolymers are produced.

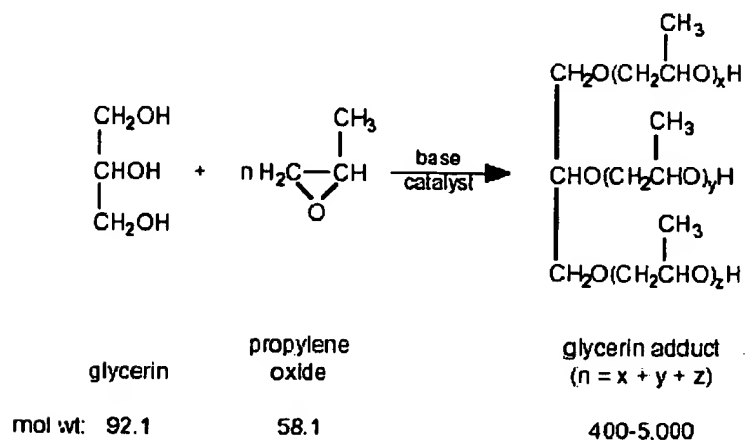
Potassium hydroxide is the basic catalyst most often employed. The initiator used depends on the type of polyurethane (i.e., flexible, rigid or nonfoam) to be produced from the polyhydric alcohol. This reaction is carried out by a discontinuous batch process at elevated temperatures and pressures and under an inert atmosphere (i.e., under a nitrogen blanket). After the desired degree of polymerization has been achieved, the catalyst is neutralized and removed by filtration. The polyol is subsequently purified and additives such as antioxidants are added.

Simplified reaction equations for the major polyurethane polyether polyols are illustrated below.

POLYPROPYLENE GLYCOL (PPG)



POLYOL ADDUCTS

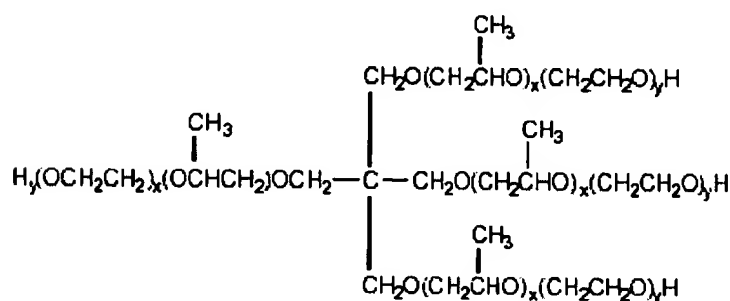


The manufacture of other polyol adducts (pentaerythritol, trimethylolpropane, trimethylolethane, sucrose and sorbitol) is similar to the above process. The manufacture of corresponding amine adducts generally follows the same process.

BLOCK COPOLYMERS

Block copolymers are commercially available that are initiated with glycerin, trimethylolethane, trimethylolpropane, pentaerythritol, sorbitol, sucrose and several other compounds. They are based almost entirely on propylene oxide; however, the secondary hydroxyl groups are capped with ethylene oxide to yield terminal primary hydroxyl groups. Since primary hydroxyl groups are more reactive than secondary hydroxyl groups, these polyols are more reactive with isocyanates.

Block copolymers can be represented by the general formula shown below, where the initiator is a polyhydric alcohol (pentaerythritol initiator is shown below).



Small quantities of mixed and alternating block copolymers are also produced. In these block copolymers the ethylene oxide is incorporated into the alkylene oxide chains. These products may also be end-capped with ethylene oxide.

Tetrafunctional block copolymers initiated with ethylenediamine are also commercially available. The amine is reacted with propylene oxide to yield the totally hydroxypropylated ethylenediamine, which is further reacted with propylene oxide and then with ethylene oxide to form the desired polyether polyol.

MODIFIED POLYOLS BASED ON PROPYLENE OXIDE

Polymer Polyols

Polymer polyols are also referred to as graft polymer polyols, graft polyols, or copolymer polyols; all of these terms are used to describe products that are basically stable dispersions of vinyl polymers in polyols. Polymer polyols are produced by the in-situ polymerization of a vinyl monomer in a base polyol.

The base polyol is typically a glycerin-initiated triol that has been end-capped with ethylene oxide (approximately 80-85% primary hydroxyl groups). Styrene and acrylonitrile are the vinyl monomers most often used. The styrene-acrylonitrile copolymers are chosen because in the preparation of graft polyols, acrylonitrile—due to its grafting tendency—provides a very important linkage between the vinyl polymer chain and the polyol chain. In addition to the graft copolymerates, the polymer polyol contains the homopolymers of styrene and acrylonitrile dispersed in unaltered polyether polyols. The styreneacrylonitrile solids content of the polyol ranges from 5% to 45%. The solids content of the polyol depends on the end-use market; those having a high solids content are used

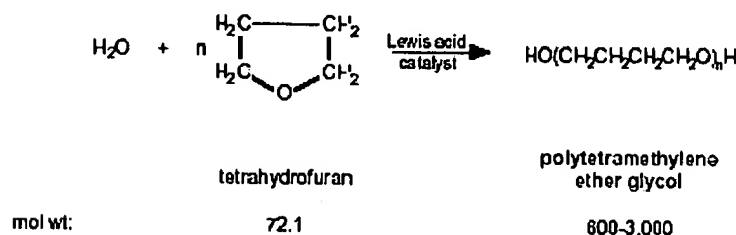
in carpet underlay while those having a lower solids content are used principally for molding applications such as automobile seating and furniture. Polymer polyols may be used alone but are typically used in blends with other highly reactive polyols in the production of high-resilience (HR) flexible foams. The principal benefits derived from the use of these materials are improved processing—due largely to a "cell opening" effect in HR applications—and enhancement of modulation, which in foams is measured as load bearing. Polymer polyols alone or in blends with conventional polyols permit the production of a range of foams with medium to high load-bearing properties. BASF, Dow, Lyondell Chemical and Olin are the primary producers of polymer polyols in the United States.

Polyurea Polyols

Another technically important group of modified polyols based on propylene oxide are the polyurea polyols, also known as PHD polyethers. Polyurea polyols are produced by the in-situ polyaddition reaction of isocyanates with amines in a base polyol. The isocyanate reacts more quickly with amines than polyols. Consequently, the isocyanate preferentially reacts with the amine (e.g., hydrazine) to form a urea group; the polyol functions only as a dispersion medium. The concentration of solids is limited by the viscosity of the product. However, polyurea solids content of 20-40% can usually be achieved. Polyurea polyols are used in blends with other highly reactive polyols in the production of HR foams and for reaction injection-molded (RIM) applications. Bayer is a producer of polyurea polyols in the United States.

POLYOLS BASED ON TETRAHYDROFURAN

Polytetramethylene ether glycol (PTMEG) of 650-2,000 molecular weight is prepared by the Lewis acid catalyzed polymerization of tetrahydrofuran.



PTMEG is, depending on its molecular weight, a liquid or a white waxy solid that melts to a clear liquid at 38°C (100°F). BASF Corporation, DuPont and QO Chemicals are the producers of PTMEG in the United States. The product is used in polyurethane elastomers and spandex fibers.

ENVIRONMENTAL ISSUES

Polyether polyols do not present an industrial hygiene problem, when used according to the relevant regulations. However, environmental issues are increasingly important in the polyurethane and polyurethane raw materials businesses. The industry has had to find replacements for HCFC blowing agents. It is now addressing the recyclability and reclaimability of used products. Some of the developing processes produce recovered polyols from polyurethane wastes.

Copyright © 2002 Synair Corporation. All rights reserved.